I. APPLICATION OF THE EQUATIONS-OF-MOTION METHOD TO THE EXCITED STATES OF N_2, CO, AND C_2H_4

II. APPLICABILITY OF SCF THEORY TO SOME OPEN-SHELL STATES OF CO, N_2, AND O_2

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ABSTRACT

In Part I various low-lying electronic states of N_2, CO, and ethylene are studied by the equations-of-motion-method. This approach attempts to describe excitation processes directly, without solving Schroedinger's equation separately for the excited and ground states. It reduces to a matrix eigenvalue problem in a space of single particle-hole excitations, and the effect of double excitations is determined by perturbation theory.

Using extensive Gaussian basis sets, excitation energies and oscillator strengths are obtained for nine states of CO and eleven states of N_2 at the equilibrium geometry. The typical error in frequency is about five per cent relative to experiment. Calculated oscillator strengths are also very good since the total intensity must very nearly satisfy the energy weighted sum rule. Results for ethylene show that the V state is a valence state but is more diffuse than the T state and ground state.

Potential energy curves are constructed for all these states by solving the equations at a few points with slightly smaller basis sets. The theory is appropriate as long as the Hartree-Fock approximation is a good one for the ground state--within about thirty per cent of equilibrium. The Σ^+ states of N_2 and CO are most interesting because questions about perturbation and pre-dissociation can be answered.

Part II describes open shell SCF calculations for some diatomic molecules. By working with the real functions π_x and π_y instead of π^+ and π^-, the SCF Hamiltonians for the Σ states of the configurations

$(\pi_u)^3(\pi_g)$, $(\pi_u)^3(\pi_g)^3$, and $(1\pi)^3(2\pi)$ of diatomic molecules can be expressed in terms of Coulomb and exchange operators only. With these results, conventional SCF programs can solve for the wavefunctions of many interesting states of N_2, O_2, and CO, e.g., the $B\ ^3\Sigma_u^-$ state of O_2. For many states, the SCF results are in good agreement with experiment. However, SCF theory runs into serious trouble if electron correlation is important in determining the relative locations of excited states.

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I. Application of the Equations-of-Motion Method to the Excited States of N_2, CO, and C_2H_4

A. Introduction

Nearly all our intuitive knowledge of chemical behavior is based on the localized chemical bond. The role of a fixed spatially directed valency in determining the size and shape of molecules was understood before quantum mechanics and, with the development of valence bond theory, most problems in chemical structure were theoretically explainable. However, quantitative ab initio calculations of bond strengths have not proven possible by this method because the definition of a valence bond wave function ignores important correlation terms in the total energy representing instantaneous electronic interactions. This problem occurs because chemical energies are really small compared to the total energy of the reactants or products and are often comparable to the correlation energy change upon reaction.

The molecular orbital approach (Hartree-Fock theory) was the first to put calculation of total molecular energies on a rigorous basis. The correlation energy can be defined as the difference between the non-relativistic experimental energy and the Hartree-Fock energy and is usually small for unexcited molecules. However, the molecular orbital picture breaks down as a molecule is significantly distorted from equilibrium and dissociation curves are often worse than would be predicted by a simple valence bond approach. Excited state wave functions can also be defined in the Hartree-Fock method but

excitation frequencies calculated in this manner are unreliable in cases where there are large correlation energy differences between molecular states (see Part II); these differences can actually affect the ordering of states of the same symmetry.

In order to answer quantitative questions about chemical bonding or excitation processes, theoretical chemists have been forced to find very accurate molecular wave functions. This is usually done in a configuration interaction (CI) calculation where a large number of excited configurations, representing electronic correlation, are mixed with the molecular orbital approximation to the wave function. Although such calculations are exact in principle, computational limitations usually require arbitrary truncation in the number of configurations included with resultant inaccuracies. All in all, we have lost most of our intuitive understanding of electronic binding in molecules in going from the valence bond model to the molecular orbital approximation to large CI calculations while, at the same time, numerical agreement with experiment is still often inadequate, especially considering the resources allocated to these calculations.

An alternative approach which is presented here is one which describes molecular excitation processes efficiently and inexpensively. It utilizes the model of an electron gas, corrected consistently for non-ideality, to describe the behavior of electrons in molecules; all the terms included are physically understandable even though they do not add to our insight in terms of classical chemical theory. Excitation frequencies and, in particular, optical oscillator strengths, are predicted accurately for small molecules, and extension to larger

systems is straightforward.

Although the mathematics of the many-body (electron gas) approach is quite tedious, involving Green's functions and second quantization, the concepts involved are simple. If a time dependent function (propagator) is sought which describes the motion of a single electron introduced into a molecule, this function can be found as an expansion in terms of the occupied Hartree-Fock orbitals (holes) and virtual orbitals (particles) where the coefficients contain matrix elements of the interelectronic coulomb interaction which represent scattering events, i.e. the interactions of the added electron with all the other electrons. This is simply time-dependent perturbation theory and the propagator is related to the total wave function for the system. In the lowest order (independent particle model) an electron introduced into any Hartree-Fock orbital remains there indefinitely. Its energy consists of kinetic and nuclear potential energy (one-body terms) and conlomb and exchange terms representing interactions with the average distribution of the other electrons, and will be a constant of motion. The range of the interelectronic force is the same as in free space since all the electrons are fixed in orbitals. Including all the higher order corrections to this model involves essentially a complete CI calculation and is not feasible. The idea of many-body theory is to include the effect of scattering events of certain types whose amplitudes are large or are likely to add coherently. This is called partial summation.

The random phase approximation is used as a starting point for the development of our theory. It involves a partial summation of

the so-called ring interactions and holds rigorously for a dense electron gas. The RPA by itself has been applied with moderate success to molecules, presumably because the strong central force of the nuclear framework gives an electron kinetic energy comparable to that in a dense electron gas limiting the characteristic time for interaction with other electrons. The type of scattering event which is considered is the creation of local excitations in the electronic medium as an electron moves through it; this polarization results in a screened force between electrons or, alternatively, a quasi particle with a smaller mass consisting of the electron with its surrounding shell of polarization. Thus the dielectric constant of the medium is greater than unity. It should be noted that the RPA only includes dynamic correlations between electrons; it does not take into account scattering of electrons by pre-existing particle-hole pairs (excitations) relative to the Hartree-Fock model and thus underestimates the correlation energy.

The equations-of-motion method of Rowe,[2] as reviewed in the next section, is a convenient way of formulating the many-body problem to consistently treat excitation processes, that is, to use the same approximations for the ground and excited states of the system under consideration. Given a level of approximation for the ground state, the excited states are generated by a series of excitations expressed in terms of the Hartree-Fock orbitals. The amplitudes for these excitations are eigenvectors of a simple matrix equation and the excitation frequencies are the eigenvalues. As will be seen, these amplitudes easily show the extent of electron correlation in an excited state. For instance, the $V(^1B_{3u})$ state of ethylene which is predominatly

a $\pi \rightarrow \pi^*$ transition from the ground state also involves excitations of a $\sigma \rightarrow \sigma^*$ type and, to a lesser extent, multiple excitations. From a many-body point of view an electronic excitation of a molecule involves a sharp decrease in the dielectric constant at the excitation frequency. Local electronic excitations are strongly coupled together because of the increased interaction, and, when the correct amount of energy is supplied, they produce a cooperative transition. In the equations-of-motion formulation, the matrix problem need only be solved in the representation of important excitations, perhaps all single particle-hole excitations or $\pi \rightarrow \pi^*$ excitations; the contribution of lesser processes can be estimated by perturbation theory.

When the ground state used in Rowe's equation is the Hartree-Fock ground state and the presence of real correlations is thus ignored, the RPA matrix equation results. If the excitation space is of size n the RPA matrix is made up of two $n \times n$ submatrices, the A matrix representing the Hamiltonian of particle-hole excitations (single excitation CI Hamiltonian) as it affects the excited state energy and the B matrix including the "virtual" correlations in the ground state. The result is equivalent to the so-called quasi-boson approximation where particle-hole pairs, once created, behave exactly like bosons, scattering into other particle-hole pairs but not interacting at all with the local density fluctuations present to a small extent in any real system. It is readily seen that this model violates the Pauli exclusion principle in that it allows electrons to move into partially occupied spin-orbitals. Also, because the RPA underestimates correlation energy and excited states are usually less correlated than the ground state,

the excitation frequencies are underestimated. For low lying states like the $T(^3B_{3u})$ state of ethylene at 3.6 eV this can result in instabilities in the equations.

The corrections to the RPA equations were worked out by Shibuya and McKoy[1] and modified by Shibuya, Rose, and McKoy[6] as described in the Appendix. They are not an attempt to perform further partial summations of interactions but are the lowest order corrections to the RPA partial summation. This theory is consistent with second order perturbation theory in the sense that all terms involving quadratic dependence in the interaction elements V_{ijkl} are retained. Thus, the limiting accuracy of the method as it is presented here is that of constructing a correlated ground state by performing a double excitation CI calculation on the Hartree-Fock wave function, performing a CI calculation on the excited state using all single and double excitations and single de-excitations from this ground state, and determining the energy difference between the states. This would be a herculian task if properly descriptive basis sets were used. By asking only for energy differences the equations-of-motion circumvents the inclusion of relatively unimportant terms and the necessity for diagonalization of large CI natrices. Transition properties are also obtained very easily and accurately in this formalism.

The correction terms can all be understood physically. The matrix T corrects the A matrix by allowing an electron to scatter from a particle state to a particle state or from a hole state to a hole state by exchanging with an electron in a real correlated configuration. Another A matrix correction proportional to the correlation density $\rho^{(2)}$,

modifies the coulomb force an electron feels in propagating through the molecule due to the presence, on the average, of local polarizations. Both of these terms help to correct the exclusion principle violations. If only the diagonal corrections to the A matrix are considered, it is equivalent to defining renormalized independent particle energies which best account for correlation effects. The correction S to the B matrix is neglected by Rowe in his higher RPA theory[2] and allows to some extent for coulomb forces between "virtual" correlations in the ground state. The D matrix is a metric which essentially insures that the eigenstates remain orthonormal.

The next section reviews the formal development of the equations-of-motion and the method of obtaining numerical solutions. The following two sections give the results of calculations for N_2, CO, and ethylene at the equilibrium configuration and slightly distorted geometries. The theory is adequate when the Hartree-Fock model is a good representation for the ground state, i.e., the molecule is a closed shell system; excitation frequencies within about five to ten per cent of experiment are obtained if the internuclear coordinates are not displaced by more than about twenty per cent from their equilibrium values. Part II is a study of SCF wavefunctions of excited states of diatomic molecules.

B. Theoretical Considerations

1. The Renormalized Equations-of-Motion

In this section we review some pertinent aspects of the solution of the equations-of-motion we have recently proposed. References 1 and 2 contain the necessary details. The variational form of the equations-of-motion states that the operator for generating an excited state $|\lambda\rangle$ from the ground state $|0\rangle$ is exactly a solution of the equation[2]

$$\langle 0|[\delta O_\lambda,\ H,\ O_\lambda^+]|0\rangle = \omega_\lambda \langle 0|[\delta O_\lambda,\ O_\lambda^+]|0\rangle \qquad (1)$$

where ω_λ is the excitation energy, $E_\lambda - E_0$, and the double commutator is defined by

$$2[A,H,B] = [A,[H,B]] + [[A,H],B] \qquad (2)$$

δO_λ is a variation on O_λ. The operator O_λ^+ is specified by a set of amplitudes which determine the relative importance of various particle-hole excitations in generating the state $|\lambda\rangle$, i.e.,

$$O_\lambda^+|0\rangle = |\lambda\rangle . \qquad (3)$$

The dominant terms in O_λ^+ are the single particle-hole amplitudes (1p - 1h). In the first approximation we restrict O_λ^+ to the 1p - 1h form

$$O^+(\lambda SM) = \sum_{m\gamma}\{Y_{m\gamma}(\lambda S)\, C^+_{m\gamma}(SM) - Z_{m\gamma}(\lambda S)\, C_{m\gamma}(\overline{SM})\} \qquad (4)$$

and then we will include the 2p - 2h contribution by a perturbation

approach. In Eq. (4) $C^{+}_{m\gamma}(SM)$ is spin-adapted particle-hole creation operator and m and γ specify a particle and a hole state respectively. With O^{+}_{λ} of Eq. (4), Eq. (1) gives the following equation[3] for the amplitudes $\{Y_{m\gamma}\}$ and $\{Z_{m\gamma}\}$ and the excitation frequency ω_{λ}

$$\begin{bmatrix} A(S) & B(S) \\ -B^{*}(S) & -A^{*}(S) \end{bmatrix} \begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix} = \omega(\lambda S) \begin{bmatrix} D & 0 \\ 0 & D \end{bmatrix} \begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix} \tag{5}$$

where the matrix elements of A, B, and D are

$$\begin{aligned} A_{m\gamma,\, n\delta}(S) &\equiv \langle 0 \,|[C_{m\gamma}(SM),\, H,\, C^{+}_{n\delta}(SM)]\,|0\rangle \\ B_{m\gamma,\, n\delta}(S) &\equiv -\langle 0 \,|[C_{m\gamma}(SM),\, H,\, C_{n\delta}(\overline{SM})]\,|0\rangle \\ D_{m\gamma,\, n\delta}(S) &\equiv \langle 0 \,|[C_{m\gamma}(SM),\, C^{+}_{n\delta}(SM)]\,|0\rangle \end{aligned} \tag{6}$$

To evaluate the matrix elements in Eq. (6) we write an approximate ground state wavefunction,

$$|0\rangle \approx N_0(1 + U)\,|HF\rangle \tag{7}$$

where

$$U = \tfrac{1}{2} \sum_{\substack{m\gamma \\ n\delta}} \sum_{S} C'_{m\gamma,\, n\delta}(S)\, C^{+}_{m\gamma}(S0)\, C^{+}_{n\delta}(\overline{S0})\ . \tag{8}$$

The approximate ground state wavefunction, $|0\rangle$, of Eqs. (7) and (8)

contains the main correlation effects for closed-shell systems.[4] We have recently shown that with $|0\rangle$ of Eq. (7) the matrix elements of Eq. (6) are, to a very good approximation[1, 5]

$$\begin{aligned}
A_{m\gamma,\,n\delta}(S) &= A^{(0)}_{m\gamma,\,n\delta}(S) + \delta_{\gamma}\left[T_{mn} - \tfrac{1}{2}(\epsilon_m+\epsilon_n-2\epsilon_{\gamma})\rho^{(0)}_{mn}\right] \\
&\quad - \delta_{mn}\left[T_{\gamma\delta} - \tfrac{1}{2}(2\epsilon_m - \epsilon_{\gamma} - \epsilon_{\delta})\rho^{(2)}_{\gamma\delta}\right] \\
B_{m\gamma,\,n\delta}(S) &= B^{(0)}_{m\gamma,\,n\delta}(S) + (-1)^S S_{m\gamma,\,n\delta} + X_{m\gamma,\,n\delta}(S) \\
D_{m\gamma,\,n\delta} &= \delta_{mn}\delta_{\gamma\delta} + \delta_{mn}\rho^{(2)}_{\gamma\gamma} - \delta_{\gamma\delta}\rho^{(2)}_{mn}
\end{aligned} \tag{9}$$

where ϵ_m is a Hartree-Fock (HF) orbital eigenvalue. The terms in Eq. (9) are defined as follows

$$\begin{aligned}
A^{(0)}_{m\gamma,\,n\delta}(S) &= \delta_{mn}\delta_{\gamma\delta}(\epsilon_m - \epsilon_{\gamma}) - V_{m\delta n\gamma} + V_{m\delta\gamma n}\delta_{S0} \\
B^{(0)}_{m\gamma,\,n\delta}(S) &= -(-1)^S V_{mn\delta\gamma} + 2V_{mn\gamma\delta}\cdot\delta_{S0}
\end{aligned} \tag{10}$$

$$\begin{aligned}
S_{m\gamma,\,n\delta} &= -\sum_{\rho\mu}\left\{V_{m\mu\delta p}C_{p\mu,\,n\gamma}(0) + V_{n\mu\gamma p}C_{p\mu,\,m\delta}(0)\right\} \\
T_{mn} &= -\tfrac{1}{2}\sum_{q\mu\nu}\left\{V_{mq\mu\nu}C^{*}_{n\mu,\,q\nu}(0) + V_{\mu\nu nq}C_{m\mu,\,q\nu}(0)\right\} \\
T_{\gamma\delta} &= \tfrac{1}{2}\sum_{pq\nu}\left\{V_{pq\gamma\nu}C^{*}_{p\delta,\,q\nu}(0) + V_{\delta\nu pq}C_{p\gamma,\,q\nu}(0)\right\}
\end{aligned} \tag{11}$$

$$\begin{aligned}
V_{ijk\ell} &= \langle i(1)\, j(2)\left|\frac{1}{r_{12}}\right|k(1)\ell(2)\rangle \\
C_{ijk\ell}(0) &= \tfrac{3}{2}\, C'_{ijk\ell}(0) - \tfrac{1}{2}\, C'_{ijk\ell}(1) \\
C_{ijk\ell}(1) &= \tfrac{3}{2} C'_{ijk\ell}(1) - \tfrac{1}{2}\, C'_{ijk\ell}(0)
\end{aligned} \tag{12}$$

In Eqs. (9)-(11) the indices m, n, p and q always refer to particle states and γ, δ, μ and ν to whole states. The matrices T and S in (11) depend linearly on both the interaction elements $V_{ijk\ell}$ and the correlation coefficients $C'_{ijk\ell}$. Only integrals of the form $V_{m\gamma n\delta}$ and $V_{mn\gamma\delta}$ are needed to compute the matrix elements in (9). The matrix X which contains interaction elements V_{mnpq} and $V_{\gamma\delta\mu\nu}$, which are not of this type, have been shown to be negligible and are not included in these calculations.[5] ϵ_m or ϵ_γ represents a Hartree-Fock (HF) orbital energy. $\rho^{(2)}_{mn}$ and $\rho^{(2)}_{\gamma\delta}$ are the second order density matrix corrections and depend quadratically on the correlation coefficients; terms containing them are part of the renormalization scheme.[6] If all correlation coefficients $C'_{ijk\ell}(S)$ are ignored the elements of (9) reduce to (10), the random phase approximation (RPA) matrices.

With these approximations to the matrix elements $A_{m\gamma,\,n\delta}$, $B_{m\gamma,\,n\delta}$ and $D_{m\gamma,\,n\delta}$, the equation of motion (5) can be solved by standard matrix algebra to yield the 1p-1h amplitudes $\{Y_{m\gamma}\}$ and $\{Z_{m\gamma}\}$ and the corresponding excitation energy ω_λ. Although the results given here are obtained from the solution of (5) accurate answers (see B. 2.) can be obtained by including only diagonal terms in the D matrix, the principal advantage being that a new eigenvalue equation (13) can be formed which has the form

$$\begin{bmatrix} \bar{A}(S) & \bar{B}(S) \\ -\bar{B}^*(S) & -\bar{A}^*(S) \end{bmatrix} \begin{bmatrix} \bar{Y}(\lambda S) \\ \bar{Z}(\lambda S) \end{bmatrix} = \omega(\lambda S) \begin{bmatrix} \bar{Y}(\lambda S) \\ \bar{Z}(\lambda S) \end{bmatrix} \tag{13}$$

where the elements of $\bar{A}$, $\bar{B}$, $\bar{Y}$, and $\bar{Z}$ have the renormalized forms

$$\bar{A}_{m\gamma, n\delta} = f^{-1}_{m\gamma} A_{m\gamma, n\delta} f^{-1}_{n\delta}$$

$$\bar{B}_{m\gamma, n\delta} = f^{-1}_{m\gamma} B_{m\gamma, n\delta} f^{-1}_{n\delta}$$

$$\bar{Y}_{m\gamma} = f_{m\gamma} Y_{m\gamma}$$

$$\bar{Z}_{m\gamma} = f_{m\gamma} Z_{m\gamma} \quad , \tag{14}$$

with

$$f_{m\gamma} = (1 + \rho^{(2)}_{\gamma\gamma} - \rho^{(2)}_{mm})^{\frac{1}{2}} \quad . \tag{14a}$$

Equation (5) is the final form of the equations-of-motion for the excitation frequencies, $\omega(\lambda)$, in the single particle-hole approximation. In this approximation the excitation operator, O^+_λ, contains only 1p - 1h creation and destruction operators, $C^+_{m\gamma}(SM)$ and $C_{m\gamma}(SM)$ respectively. These excitations are from a correlated ground state. Note that the equations are designed so that the matrix elements needed are ground state expectation values of double commutators. These should depend on relatively simple properties of the wavefunction. Since these double commutators, e.g., $A_{m\gamma, n\delta}$ and $B_{m\gamma, n\delta}$, are of lower particle rank than matrix elements such as $\langle 0|H|0\rangle$ they are correspondingly less sensitive to the details of $|0\rangle$.

In principle one can solve Eq. (13) and the equation defining the ground state

$$O_\lambda |0\rangle = 0 \quad \text{for all } \lambda \tag{15a}$$

self-consistently. In Ref. 5 we showed that Eq. (15a) leads to the approximate conditions

$$Z_{m\gamma}(\lambda S) \cong \sum_{n\delta} C^*_{m\gamma,\, n\delta}(S)\, Y_{n\delta}(\lambda S) \tag{15b}$$

$C_{m\gamma,\, n\delta}$ is defined in Eq. (12). In practice Eq. (15) can be solved only approximately but this is a minor point since, as expected, the calculated excitation frequencies are not sensitive to small changes in the correlation coefficients $\{C'_{m\gamma,\, n\delta}\}$, Eq. (8). In the calculations presented here we solve (5) iteratively using the amplitudes $\{Y_{m\delta}\}$ and $\{Z(m\delta)\}$ in (15) to determine the correlation coefficients for a new iteration until the eigenvectors and eigenvalues have converged. However, an initial approximation to the coefficients $C'_{ijk\ell}$ using Rayleigh-Schroedinger perturbation theory gives essentially the converged result. Note that the particle-hole pairs $\{m\gamma\}$ determine the 2p - 2h components which should be included in the ground state $|0\rangle$.

Generally the most important components of low-lying excited states are the single-particle-hole pairs. In the complete expansion of the excitation operator O^+_λ, Eq. (4), these would have the largest amplitudes. However doubly excited configurations (relative to the ground state)--two particle-hole components--can affect the excitation energies of some molecular states by more than three electron volts, the actual amount reflecting mainly a self-consistent readjustment of the core of basically ground-state (hole) orbitals during the excitation process. In Ref. 6 we showed how the theory including two-particle-like states is equivalent to the single-particle-like theory with a renormalized interaction and suggested a perturbation approximation for including

their effects on the excitation frequencies and transition moments. The main thrust of the argument is that if $\{ Y_{m\gamma} \}$ and $\{ Z_{m\gamma} \}$ are the amplitudes of the 1p - 1h components in O_λ^+ then the excitation frequency of this transition is, to a good approximation,

$$\omega = \omega^{(1p-1h)} - \Delta\omega \tag{16}$$

where $\omega^{(1p-1h)}$ is the excitation energy of the 1p - 1h approximation, i.e., an eigenvalue of Eq. (13) and

$$\Delta\omega = \tilde{Y}^* \underset{\sim}{\Delta_a} \tilde{Y} + \tilde{Z}^* \underset{\sim}{\Delta_d} \tilde{Z} \tag{17}$$

The elements of the matrices $\underset{\sim}{\Delta_a}$ and $\underset{\sim}{\Delta_d}$ are given explicitly in Eqs. (46) and (47) of Ref. 6 but they are essentially perturbation-like matrix elements in which the numerator is a matrix element of the Hamiltonian between a 1p - 1h and 2p - 2h component. The denominators are particle-hole energy differences. Actually the inclusion of 2p - 2h terms can be viewed as consistent with an expansion of the equation-of-motion Eq. (5) to second order (see Section B2). We refer to the excitation frequencies of Eq. (16) as those of the equations-of-motion including 1p - 1h and 2p - 2h components.

Finally in the 1p - 1h theory the transition moment matrix element between a state $|\lambda\rangle$ and the ground state $|0\rangle$ is given, to the same accuracy as equation (5) (to second order), as

$$M_{o\lambda} = \langle 0 | M | \lambda \rangle = \sqrt{2} \cdot \sum_{m\gamma} [Y^*_{m\gamma}(\lambda)\, M_{m\gamma} + Z^*_{m\gamma}(\lambda)\, M_{m\gamma}] \tag{18a}$$

$$M_{m\gamma} = M^o_{m\gamma} + \sum_\delta M^o_{m\delta}\, \rho^{(2)}_{\gamma\delta} - \sum_n M^o_{n\gamma} \rho^{(2)}_{mn} \tag{18b}$$

$M^0_{m\gamma}$ is the transition moment between a hole orbital γ and a particle orbital m and $\rho^{(2)}_{mn}$ and $\rho^{(2)}_{\gamma\delta}$ are defined in (9). The two last terms in Eq.(18b) represent second order corrections to $M_{o\lambda}$ and tend to alter (usually decrease) it by only a few percent. Other second order corrections due to 2p - 2h components are not included here. They depend only on particle-particle (M_{mn}) and hole-hole ($M_{\gamma\delta}$) transition moments and should be of lesser magnitude. Many sum rules, including those for the oscillator strength and rotational strength must be very nearly satisfied in this method.[7] In terms of $M_{o\lambda}$ the oscillator strength, f, of the transition is

$$f = \tfrac{2}{3} \cdot G \cdot \Delta E \cdot M^2_{o\lambda} \quad . \tag{19}$$

where G is the degeneracy factor.

In the following sections we discuss the results of calculations on various states of N_2, CO, and C_2H_4 using the 1p - 1h theory, Eq. (5), and the 1p - 1h and 2p - 2h theory, Eq. (16).

2. Empirical Justification of the Expansion

Although the "equation-of-motion" (1) is exact in principle, it must be truncated in any practical calculation. Errors can occur through limiting the basis set and the set of MO's used in the calculation or in the formal expansion of (1). This latter difficulty does not occur in a complete CI calculation but restricting the configurations included amounts to a similar but more arbitrary approximation. The expansion to "second order" used in obtaining (5) is consistent with a type of perturbation theory at least from a heuristic point of view, as is the derivation of the Eq. (17) for 2p - 2h corrections. The resulting matrix equations are of low dimensionality even when an extensive basis set must be employed.

In second quantization formalism the many electron Hamiltonian can be written as

$$H = H_1 + H_2 + H_3 \tag{20}$$

$$H_1 = \sum_i \epsilon_i n_i$$

$$H_2 = -\sum_{i\gamma} (2J_{i\gamma} - K_{i\gamma}) n_i + \tfrac{1}{2}\sum_{ij} (J_{ij} n_j - K_{ij}) n_i + \sum_{ij} K_{ij} C_{ij}^{+}(00) C_{ji}^{+}(00)$$

$$H_3 = -\sum_{ij} (1-\delta_{ij}) \Big[\sum_j (2V_{i\gamma j\gamma} - V_{i\gamma\gamma j}) + \tfrac{1}{2}\sum_k V_{ikkj}\Big] \sqrt{2} \times C_{ij}^{+}(00) + \sum_{ijk\ell} (1 - \delta_{ik}\delta_{j\ell})(1 - \delta_{i\ell}\delta_{jk}) V_{ijk\ell}\, C_{ik}^{+}(00)\, C_{j\ell}^{+}(00)$$

$$J_{ij} = V_{ijij}$$

$$k_{ij} = V_{iijj}$$

$$n_i = \sqrt{2}\, C_{ii}^{+}(00)$$

The notation is the same as in the text with J_{ij} and K_{ij} being coulomb and exchange integrals and n_i being a space orbital number operator. In the Rayleigh-Schroedinger perturbation scheme H_1 is the zero order Hamiltonian H_0 and H_2 and H_3 are the diagonal and off-diagonal terms of the perturbation H'. Grimaldi[27] has shown that this perturbation scheme gives accurate correlation coefficients for the ground states of N_2 and CO using only second order energy corrections. A reasonable approach to solving (1) would then be to consider the correlation coefficients $C'_{ijk\ell}$ as first order terms since they are first order corrections to the ground state wavefunction. Expansion (5) then includes all terms of the form $(V_{ijk\ell})^m (C'_{ijk\ell})^n$, where $m + n \leq 2$, and is thus analogous to a Rayleigh-Schroedinger expansion of the excitation energy through second order. Similar arguments can be made for dropping interaction terms in the double excitation matrix elements. Use of another scheme such as chosing the zero order Hamiltonian as $H_1 + H_2$ of (20) would be more difficult to implement. Furthermore we find that the discrepancy between the eigenvalues obtained in these two schemes would be less than about five per cent if double excitations are handled consistently. However it can be much greater if only the (1p - 1h) theory is used.

Of the various approximations made in the previously published SHRPA scheme[5] (summarized in Section C. 3 in text) only the one which involves setting $C'_{ijk\ell}(0) = C'_{ijk\ell}(1)$ is exceptionally poor. Although this is true identically if i = k or j = ℓ the difference for the smaller off-diagonal coefficients is important since singlet and triplet excitation frequencies are affected predominately by the singlet or triplet

coefficients, respectively. Thus the T state of ethylene which should be adequately described by the [3s2p/1s] basis of Ref. 5 decreases in energy by 0.9 eV when the [4s2p/2s]+R($3P_zC$) basis us used in the original SHRPA scheme. However, when calculations are done in both bases using the correct equations (9) the change is only 0.2 eV. The idea of including only correlation coefficients generated from the same symmetry as the excitation under consideration is reasonable if these represent a large portion of the correlation energy, e.g., 60% in the case of the B_{3u} symmetry of ethylene. Inclusion of all the coefficients increases the B_{3u} frequencies by less than 0.4 eV. In N_2 or CO there are many low-lying states of different symmetries and all the coefficients must be included.

Renormalization of the equations as outlined in Ref. (6) involves inclusion of terms in the second order correction to the matrix A which are proportional to the second order density matrix and also inclusion of the matrix D. These effects tend to cancel causing a typical excitation frequency of a valence state to decrease less than 5%. The greatest effect was found for the $a^3\Pi$ state of CO where renormalization decreased the frequency by 8%. Treating $\underset{\sim}{D}$ as diagonal (13) is a very good approximation affecting the frequencies by less than 1%.

Finally iterating the solutions to self-consistency is of minor importance. One iteration is sufficient to converge the frequencies to the final answer which, in N_2 or CO, is only about 0.1 eV or less above that using the initial (Rayleigh-Schroedinger) correlation coefficients $C'_{ijk\ell}$. In accordance with these observations, an argument could be made for not iterating the solutions to self-consistency. In ethylene the T and V states increase in energy

about 0.2 eV upon iteration, and at convergence sigma-pi correlation is larger and pi correlation is smaller relative to the Rayleigh-Schroedinger guess.

3. Choice of Basis Functions

The set of Gaussian functions to be employed in the calculations is the most important practical consideration if optimal accuracy is to be obtained at minimal cost. A [4s3p] contracted Gaussian basis using a (9s5p) primitive atomic set[28] gives very good agreement with experiment if supplemented with diffuse functions. This type of basis set was used for the equilibrium configuration calculations on N_2, CO, and C_2H_4 reported in Section C.

d functions are relatively unimportant, affecting the frequencies by several tenths of an eV in N_2 for instance. The contracted valence functions were those of Dunning.[28] For ethylene we used the [4s2p/2s] + R($3p_z$C) basis. The diffuse pπ functions on the carbon atoms have exponents ζ = 0.0365, 0.0116, and 0.0037. For the CO the basis is a [4s3p] valence set plus a single diffuse s function on carbon and oxygen (ζ = 0.036 and ζ = 0.048) and a diffuse p_z function on each center (ζ = 0.030 and 0.040). In N_2 we used a [4s3p] valence basis plus two p_z functions (ζ = 0.05 and 0.01) and two dπ functions (ζ = 0.3 and 0.03) at the center of the molecule. This is necessary to describe the c′ $^1\Sigma_u^+$, b′ $^1\Sigma_u^+$ and b $^1\Pi_u$ states. The importance of diffuse functions in the final frequency ranges from about 0.3 eV for the V state of ethylene and 1.5 eV for the b′ state of N_2 to several eV for the c′ state of N_2 and the B and C states of CO. All these states are somewhat diffuse.

In practice we have taken only the lowest 19 virtual orbitals in solving the equations-of-motion for N_2 and CO at the equilibrium internuclear distance. Only for the $^1\Sigma^+$ states of CO was it necessary

to further truncate the particle-hole basis (from 32 to 30) to utilize existing programs. Neither truncation has a significant effect on the excitation energies since representative valence and diffuse virtual orbitals are included accounting for about half the total ground state correlation energy. For ethylene we used a more efficient transformation program which included 22 of 26 virtual orbitals. To keep the total cost of a calculation small for molecules of low symmetry reasonable--let us say under 1 hour--it is necessary at present to restrict the total number of MO's to about 30.

In section D we report results for all three molecules in slightly distorted geometries. Here it was found that a [3s2p] basis set contracted from a (7s3p) primitive set[29] gives good answers for CO and C_2H_4 while it is not sufficient for N_2, either in the Hartree-Fock approximation or the excitation process, due to the high symmetry which restricts mixing of configurations. Also, although the sum rule for oscillator strengths is nearly obeyed, the distribution of intensity among the states is very dependent on the nature of the diffuse functions employed. For instance, the B and C states of CO have much lower intensities when extra diffuse functions are placed at the center of the molecule. Excellent agreement with experiment for Rydberg state intensities should not be expected unless a very diffuse and balanced basis is used; thus the apparent better accuracy of the oscillator strengths of these states in Section C.2. is probably fortuitous.

C. Results at Equilibrium Geometry

1. States of N_2

The electron configuration of the ground state of N_2 is

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(\pi_{ux})^2(\pi_{uy})^2(3\sigma_g)^2 \ .$$

We have considered the following states: B $^3\Pi_g(3\sigma_g \rightarrow \pi_g)$, a $^1\Pi_g$ $(3\sigma_g \rightarrow \pi_g)$, A $^3\Sigma_u^+$, b $^1\Sigma_u^-$, B $^3\Sigma_u^-$, a′ $^1\Sigma_u^-$, W $^3\Delta_u$, and w $^1\Delta_u$ [all $(\pi_u \rightarrow \pi_g)$, c′ $^1\Sigma_u^-$ $(3\sigma_g \rightarrow 3\sigma_u)$, C $^3\Pi_u$ $(2\sigma_u \rightarrow \pi_g)$, and b $^1\Pi_u$ $(2\sigma_u \rightarrow \pi_g)$. We indicate in parentheses the electron configuration of the principal component of each state.

The first step of the calculation is to carry out a Hartree-Fock calculation in order to generate a particle-hole basis. The occupied orbitals are hole states and the virtual orbitals are particle states. The SCF calculations are done in a basis of Gaussian orbitals on each atom. The size of the basis determines the quality of the hole states and the number of particle states. We used a [4s3p] basis of contracted Gaussian functions plus some diffuse components; details are given in the Appendix. Table I lists the hole and particle energy levels used in the calculation.

We include excitations out of all hole levels except the $1\sigma_g$ and $1\sigma_u$ levels. These levels are too low to have any effect on the low-lying excited states we consider. All particle-hole excitations of the appropriate symmetry are included in the calculation on each state. These particle-hole pairs,

TABLE I. SCF molecular orbital eigenvalues for N_2[a]

MO		ϵ_γ	MO		ϵ_m	MO		ϵ_m
1	$1\sigma_g$	-15.7079	8[b]	$3\sigma_u$	0.0257	20	$5\sigma_g$	0.8602
2	$1\sigma_u$	-15.7043	9	$1\pi_{gx}$	0.0910	21	$6\sigma_u$	1.0232
3	$2\sigma_g$	- 1.5255	10	$1\pi_{gy}$	0.0910	22	$7\sigma_u$	1.5413
4	$2\sigma_u$	- 0.7727	11	$4\sigma_u$	0.1632	23	$4\pi_{gx}$	1.6651
5	π_{ux}	- 0.6240	12	$2\pi_{gx}$	0.1654	24	$4\pi_{gy}$	3.6651
6	π_{uy}	- 0.6240	13	$2\pi_{gy}$	0.1654	25	$3\pi_{ux}$	3.0148
7	$3\sigma_g$	- 0.6271	14	$2\pi_{ux}$	0.5320	26	$3\pi_{uy}$	3.0148
			15	$2\pi_{uy}$	0.5320	27	$8\sigma_u$	3.0819
			16	$4\sigma_g$	0.5460	28	$6\sigma_g$	3.3528
			17	$5\sigma_u$	0.5869	29	$5\pi_{gx}$	3.9962
			18	$3\pi_{gx}$	0.6114	30	$5\pi_{gy}$	3.9962
			19	$3\pi_{gy}$	0.6514	31	$9\sigma_u$	33.2482
						32	$7\sigma_g$	33.5275

[a]In a $([4s3p] + R(2p_z + 2d_\pi)_{CM})$ basis of contracted Gaussians. This basis gives E_{SCF} = -108.888 a.u. See Section 3.B. for details.

[b]Orbitals 8 - 13 are diffuse functions.

in turn, determine the pair correlations--2p - 2h components of the correlated ground state--which are included in the correlation function U of Eq. (8). From Eq. (5) it would seem that if N particle-hole pairs are included then the resulting equations give an unsymmetric 2N× 2N matrix. It is well-known, however,[8] that the eigenvalues, ω, can be found by solving an N × N matrix for the eigenvalue ω^2. The largest matrices which we have to handle are, on the average, of dimensionality 25× 25 to 30× 30. With the 1p - 1h pairs specified, Eq. (13) and Eq. (15b) can then be solved for the excitation frequencies in the 1p - 1h approximation. These eigenvalues are the aproximate excitation energies of the excited states of the system under the condition that these excited states differ only by single particle-hole excitations relative to a correlated ground state. In the next stage of the calculation we introduce the effect of 2p - 2h excitations out of the correlated ground state. We include this effect by using the approximate results, Eq. (17), for the energy lowering of the 1p - 1h frequency, due to these 2p - 2h components. For each state all 2p - 2h excitations derivable from the set of single particle-hole excitations, i.e., $\{C^+_{m\gamma}\}$ are included.

Table II shows the results of calculations on eleven states of N_2. All these calculations were done at the ground state equilibrium internuclear distance of 2.068 a.u. In the first column we list the symmetry and the conventional spectroscopic designation of the various states. The next column shows the number of single particle-hole pairs used in setting up the equations-of-motion. The excitation frequencies in the 1p - 1h approximation are listed in the third column.

TABLE II. Equations-of-Motion Calculations: Excited States of N_2 [a]

State	N [c]	ΔE [d] (1p - 1h)	ΔE [d] (1p - 1h) + (2p - 2h)	Exp [d]	% Error [e]
$B\ ^3\Pi_g(3\sigma_g \rightarrow \pi_g)$ [b]	15	9.6	7.5	8.1 [h]	7
$a\ ^1\Pi_g$ [f]	15	11.5	8.8	9.3	5
$A\ ^3\Sigma_u^+(\pi_u \rightarrow \pi_g)$	20	8.4	7.8	7.8	~0
$B'\ ^3\Sigma_u^-$ [g]	8	11.3	10.2	9.7	6
$W\ ^3\Delta_u$		10.1	9.4	8.9 [i]	6
$a'\ ^1\Sigma_u^-$	8	11.3	10.6	9.9	6
$\omega\ ^1\Delta_u$		12.0	11.0	10.3	6
$b'\ ^1\Sigma_u^+$	20	16.8	15.0	14.4 [j]	4
$c'\ ^1\Sigma_u^+(3\sigma_g \rightarrow \sigma_u)$		15.5	12.1	12.9	6
$C\ ^3\Pi_u(2\sigma_u \rightarrow \pi_g)$	10	13.3	10.8	11.1	4
$b\ ^1\Pi_u$	10	17.4	14.0	12.8	9

[a] all calculations done at an equilibrium internuclear distance of 2.068 a.u.

[b] indicates the main component of the excitation relative to the ground state.

[c] number of single particle-hole pairs used in the calculation. See Sect. B.3 for discussion of the basis set and selection of the particle-hole excitations.

[d] in electron volts.

[e] relative to the experimental value.

[f]same designation as in the previous state.

[g]the next five states have the same principal 1p - 1h component type.

[h]The experimental results for this state and for the a $^1\Pi_g$, A $^3\Sigma_u^+$, B $^3\Sigma_u^-$, a′ $^1\Sigma_u^-$, ω $^1\Delta_u$, and C $^3\Pi_u$ states are those reported by W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. 142, 1227 (1965). Their tabulations are based on high resolution optical data.

[i]W. Benesch and K. A. Saum, J. Phys. B: Atom. Molec. Phys. 4, 732 (1971).

[j]The experimental results for the b′ $^1\Sigma_u^+$, C $^3\Pi_u$ and b $^1\Pi_u$ states are from the electron energy-loss spectrum of Ref. 10.

Comparison with the experimental vertical excitation energies show that this approximation predicts all the states to lie about one to three eV's above the experimental values. Inclusion of 2p - 2h components lowers the 1p - 1h excitation frequencies by about one to three electron-volts resulting in excitation energies in good agreement with the experimental values. The percentage errors of calculated excitation energies relative to the experimental values are in the range of one to nine percent with an average error of about five per cent. The experimental results are probably reliable to within a few per cent, while we believe that the various approximations made in deriving the final equation may lead to an error of the same order. We do not intend to make any extensive comparisons between our calculated values and those obtained by other methods, e.g., SCF or CI calculations. The prime purpose of our calculations is to test the practicality and accuracy of the equations-of-motion method. The total amount of computing time is quite low. The calculations on all eleven states of N_2 required only about 20 minutes on an IBM 370/155. A typical breakdown of this time would be: 30% for the HF calculation on the ground state, 45% for the 1p - 1h calculation and 25% for the inclusion of the 2p - 2h components. The other calculations reported here i.e., on CO and C_2H_4, both required less than twice this time.

In Table III we compare the calculated oscillator strengths with available experimental results. The calculated oscillator strengths in

TABLE III. Oscillator strengths for transitions in N_2.

Transition	f_{el} [a]	$q_{v'v''}$ [b]	$f_{el} \cdot q_{v'v''}$	exp
$X\ ^1\Sigma_g^+ \rightarrow c'\ ^1\Sigma_u^+$	0.11	$q_{00} \sim 1$ [c]	0.11	0.14 ± 0.04 [d]
				0.16 [e]
$X\ ^1\Sigma_g^+ \rightarrow b\ ^1\Pi_u$	0.64	--	--	< 0.3 [f]
$X\ ^1\Sigma_g^+ \rightarrow b'\ ^1\Sigma_u^+$	0.49	--	--	large "measured" f_{el} [g]

[a] $f_{el} = \frac{2}{3} \cdot G \cdot \Delta E \cdot M^2$, where M is the dipole transition matrix element and G the degeneracy factor. The oscillator strengths in this column do not include any Franck-Condon factors.

[b] Franck-Condon factors for the v′ and v″ levels.

[c] Ref. 9.

[d] This is the measured f value for the 0 - 0 transition. See Ref. 9.

[e] Total f-value from lifetime measurements by J. E. Hesser, J. Chem. Phys. 48, 2518 (1968).

[f] See text. This is an estimate derived from the band oscillator strength measurements by the authors of Ref. 9.

[g] Weak due to intensity perturbations by v′ = 5 and 6 of the $c'\ ^1\Sigma_u^+$ and v′ = 0 of the $e'\ ^1\Sigma_u^+$ states. From shock-heated vibrationally excited N_2 f_{el} (v″ = 5 → v′ = 2) ≈ 0.83 and f_{el}(v″ = 8 → v′ =2) ≈ 0.4 [J. P. Appleton and M. Steinberg, J. Chem. Phys. 46, 1521 (1967)].

the second column of Table III do not contain any Franck-Condon factors. For transitions between states with very similar equilibrium internuclear distances and in the absence of perturbations by the vibrational levels of other states we can expect the Franck-Condon factor for the 0—0 transition to be very close to unity. This is the case for the transition $X\ ^1\Sigma_g^+ - c'\ ^1\Sigma_u^+$. Assuming a Franck-Condon (FC) factor of unity our calculated oscillator strength of 0.11 is in very good agreement with the measured values which lie in the range 0.14 ± 0.04.[9] It is well-known that it is difficult to estimate FC factors for the $X - b\ ^1\Pi_u$ transition because of strong perturbations of the vibrational levels of the $b\ ^1\Pi_u$ well by those of the $c\ ^1\Pi_u$ well.[9] However we can show that the calculated vertical electronic oscillator strength of 0.32 for the $X \rightarrow b\ ^1\Pi_u$ is in good agreement with available experimental data. Geiger and Schroeder's[10] high resolution electron energy-loss spectrum shows[9] that the 965 Å band (12.84 eV), the 0 - 4 component of the $X \rightarrow b\ ^1\Pi_u$ transition, accounts for 14% of the dipole oscillator strength in the 11.4 — 13.6 eV range. From their measured absolute value of f(965 Å) = 0.055, Lawrence et al.,[9] could then show that the total dipole oscillator strength for the 11.4 - 13.6 eV region of the spectrum is 0.40. Almost all the intensity in this region of the spectrum comes from the $c'\ ^1\Sigma_u^+$, $b\ ^1\Pi_u$, and $c\ ^1\Pi_u$ transitions. But the measured contribution of the $c'\ ^1\Sigma_u^+$ state to the total f-value is 0.14 ± 0.04 and hence the total f-value of the $b\ ^1\Pi_u$ and $c\ ^1\Pi_u$ states lies between 0.22 and 0.30.[11] The $X \rightarrow b\ ^1\Pi_u$ transition accounts for a large fraction of this total.[12] This is in fair agreement with a calculated value of 0.64 for the $X \rightarrow b\ ^1\Pi_u$ transition if we assume a constant transition moment and sum over the whole band.

Finally we obtain a vertical electronic oscillator strength of 0.49 for $X\,^1\Sigma_g^+ \rightarrow b'\,^1\Sigma_u^+$ transition. There are no reliable measured values for this transition. However the data of Ref. 10 show that the intensity of this vertical transition is very low indicating that the effective FC factor for the transition is small. This is probably due to intensity perturbations of the $b'\,^1\Sigma_u^+$ levels by those of the $c'\,^1\Sigma_u^+$.

2. States of CO

The electron configuration of the ground state of CO is

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2 \quad .$$

We have done calculations on these states: a $^3\Pi$ $(5\sigma \rightarrow 2\pi)$, A $^1\Pi$ $(5\sigma \rightarrow 2\pi)$, a' $^3\Sigma^+$, c $^3\Sigma^-$, I $^1\Sigma^-$, d $^3\Delta$, D $^1\Delta$ [all $(1\pi \rightarrow 2\pi)$], B $^1\Sigma^+$ $(5\sigma \rightarrow \sigma)$, and C $^1\Sigma^+$ $(5\sigma \rightarrow \sigma)$. The electron configuration of the principal component of each state is shown in parentheses. All calculations were done at an internuclear distance of 2.132 a.u. Table IV shows the hole and particle energy levels used in the calculation. The basis set used in the calculation is described in Section B.3.

Table V shows the results of calculations on nine states of CO. In the first column we list the symmetry and the conventional spectroscopic designation of the various states. The number of particle-hole pairs used in each calculation is listed in the next column. In the third and fourth column we show the calculated vertical excitation energies. The results in the third column are those in which only 1p - 1h excitations out of the ground state are included in the excitation operator O_λ^+. As in the results for N_2 the excitation energies in this approximation are about one to two eV's above the experimental values. Inclusion of 2p - 2h components lowers these values leading to calculated excitation energies in good agreement with experiment. These results and the experimental values are shown in columns four and five respectively of Table V. The percentage errors of calculated excita-

TABLE IV. SCF molecular orbital eigenvalues for CO[a]

MO		ϵ_γ	MO		ϵ_m	MO		ϵ_m
1	1σ	-20.6903	8[b]	6σ	0.0711	19	$4\pi_y$	0.8402
2	2σ	-11.3945	9	7σ	0.0817	20	12σ	0.8784
3	3σ	- 1.5665	10	$2\pi_x$	0.1198	21	13σ	1.1629
4	4σ	- 0.8006	11	$2\pi_y$	0.1198	22	14σ	1.7874
5	$1\pi_x$	- 0.6493	12	8σ	0.1639	23	15σ	2.2186
6	$1\pi_y$	- 0.6493	13	9σ	0.2990	24	$5\pi_x$	2.1089
7	5σ	- 0.5594	14	$3\pi_x$	0.4109	25	$5\pi_y$	2.1089
			15	$3\pi_y$	0.4109	26	$6\pi_x$	4.0880
			16	10σ	0.4376	27	$6\pi_y$	4.0880
			17	11σ	0.7686	28	16σ	4.4496
			18	$4\pi_x$	0.8402	29	17σ	23.8040
						30	18σ	43.3068

[a]In a ([4s3p] + R (p_z + s)) basis of contracted Gaussians. This basis gives E_{SCF} = -112.6986 a.u. See Section B.3. for details.

[b]Orbitals 8, 9, 12, and 13 are diffuse functions.

TABLE V. Equations-of-Motion Calculations: Excited States of CO[a]

State	N[c]	ΔE[d] (1p - 1h)	ΔE[d] (1p - 1h) + (2p - 2h)	Exp[d]	% Error[e]
a $^3\Pi$ ($5\sigma \rightarrow 2\pi$)[b]	22	7.1	6.0	6.3[h]	3
A $^1\Pi$[f]	22	10.3	8.5	8.4	~0
a' $^3\Sigma^+$ ($1\pi \rightarrow 2\pi$)	30	9.3	7.9	8.4	6
e $^3\Sigma^-$[g]	8	11.5	9.5	9.7	2
d $^3\Delta$		10.5	8.9	9.2	3
I $^1\Sigma^-$	8	11.5	9.8	9.9	1
D $^1\Delta$		12.0	10.0	10.5	5
B $^1\Sigma^+$ ($\sigma \rightarrow \sigma^*$)	30	13.8	11.4	10.8	6
C $^1\Sigma^+$ ($\sigma \rightarrow \sigma^*$)		13.4	11.4	11.4	~0

[a]All calculations done at an equilibrium internuclear distance of 2.132 a.u.

[b]indicates the main component of the excitation relative to the ground state.

[c]number of single particle-hole pairs used in the calculation. See the Appendix for a discussion of the basis set and selection of the particle-hole excitations.

[d]in electron volts.

[e]relative to the experimental value.

[g]the next four states have the same principal component.

[h]The experimental results for the A $^1\Pi$, B $^1\Sigma^+$, and C $^1\Sigma^+$ states

are from the electron energy-loss spectrum of V. Meyer, A. Skerbele, and E. Lassettre, J. Chem. Phys. 43, 805 (1965). The experimental results for the other states are from G. Herzberg, T. Hugo, S. Tilford, and J. Simmons, Can J. Phys. 48, 3004 (1970).

tion energies relative to the experimental values are in the range of one to six percent with an average error of about 3%. In terms of computer requirements the method is quite economical. For example the largest matrices involved are of the order of 30×30. Calculations using other methods have been carried out on various states of CO.[13] We do not want to make extensive comparisons between our values and those of other methods since we primarily want to test the practicality of our method. We note however that our calculated excitation energies are in as good--in many cases better--agreement with experiment as those of the CI calculations of Ref. 13. The CI calculations involve much larger matrices than those in the equations-of-motion method.

In Table VI we compare our calculated oscillator strengths with available experimental data. The $X\ ^1\Sigma^+ \rightarrow A\ ^1\Pi$ transition has been extensively studied by electron energy-loss spectroscopy. Lassettre et al.,[14] obtained a value of 0.043 for the $v' = 2$ level of the $A\ ^1\Pi$ state by extrapolating the generalized oscillator strength to zero momentum transfer. The calculated value of 0.052 for this transition is in good agreement with their result.[14] The total f-value for the $X\ ^1\Sigma^+ \rightarrow A\ ^1\Pi$ transition obtained from lifetime measurements[15] is 0.15. To obtain this value they[15] included the r-centroid dependence of the electronic transition moment in analyzing Hesser's lifetime measurements.[16] If this dependence is neglected the total f-value for the transition is about 0.094.[16] Our calculated estimate of 0.22 for the total f-value of this transition--assuming a constant electronic transition moment for transitions to the $v' = 0 \rightarrow v' = 6$ levels--could be improved by including the variation with distance (see Sec. D.2).

TABLE VI. Oscillator strengths for transitions in CO

Transition	f_{el} [a]	$q_{v'v''}$ [b]	$f_{el} \cdot q_{v'v''}$	exp
$X\ ^1\Sigma^+ \rightarrow A\ ^1\Pi$	0.22	$q_{20} \approx 0.24$ [c]	0.053	0.043 [d]
				0.15 [e]
$X\ ^1\Sigma^+ \rightarrow C\ ^1\Sigma^+$	0.12	$q_{00} \sim 1$ [f]	0.12	0.16 [g]
$X\ ^1\Sigma^+ \rightarrow B\ ^1\Sigma^+$	0.048	$q_{00} \sim 1$ [f]	0.048	0.016 [g]
$X\ ^1\Sigma^+ \rightarrow B$ and $C\ ^1\Sigma^+$			0.17	0.18 [h]

[a] $f_{el} = \frac{2}{3} \cdot G \cdot \Delta E \cdot M^2$, where M is the dipole transition matrix element and G the degeneracy factor. The oscillator strengths in this column do not include any Franck-Condon factors.

[b] Franck-Condon factors for the v′ and v″ levels.

[c] P. H. Krupenie, Natl. Std. Ref. Data Ser., Natl. Bur. Std. (U.S.) 5, (1966).

[d] This is the measured value for the $v' = 0 \rightarrow v'' = 2$ transition. See Ref. 13.

[e] This is the total f-value for the transition see Ref. 14. This value takes into account the r-centroid dependence of the electronic transition moment. See text. Lassettre[13] obtains 0.19 from electron impact studies.

[f] See Ref. 14.

[g] electron impact studies of Lassettre.[14]

[h] This is the total f-value for the $X \rightarrow B$ and $X \rightarrow C$ transitions. See text for discussion.

Finally the calculated f-value of 0.12 for the X → C transition is in good agreement with the measured value of 0.16. This value is obtained by extrapolating the generalized oscillator strength to zero momentum transfer.[14] The agreement for the X → B transition is not as good. The calculated value is 0.048 while Lassettre's extrapolation of his electron-impact results gives 0.016. These transitions are quite close to each other with the B state lying 0.6 eV below the C state. Their data[14] also show that the Born approximation is not valid for the X → B transition even at incident electron energies of 400 eV.[17] Note that the calculated total f-value for the X → B and X → C transitions is 0.17, in good agreement with their measured value of 0.18. To study these measurements more closely we plan to calculate the generalized oscillator strength as a function of momentum transfer in the Born approximation using the equations-of-motion method. Similar calculations on electron-helium scattering by Schneider have given accurate results.[18]

3. The T and V States of Ethylene

We have done additional calculations on the T and V states of ethylene which are the triplet and singlet states arising primarily from a $\pi \rightarrow \pi^*$ transition. In these calculations we use an extensive Gaussian atomic orbital basis with diffuse π^* components which is described in Section B. 3. In reference 5 we studied these same transitions in a smaller basis but we made two restrictive approximations in solving Eq. (5) (the SHRPA approximation of Ref. 5). First we included only those correlation coefficients in Eq. (8) made up of particle-hole pairs of the same symmetry as the excited state under study, in this case[19] B_{3u}. In this approximation we assumed that off-diagonal correlation coefficients were small so that $C'_{m\gamma,\, n\delta}(0) = C'_{m\gamma,\, n\delta}(1)$. Secondly, we did not use the fully renormalized matrix elements of Eq. (9), which include terms quadratic in the coefficients $C'_{m\gamma,\, n\delta}$. These terms are of the same order as other terms linear in $C'_{m\gamma,\, n\delta}$ and an interaction matrix element $V_{ijk\ell}$. These assumptions, which work reasonably well for ethylene, are poor when applied to systems with stronger electron correlation in the ground state, especially for states of symmetries that are unimportant in the correlation function, Eq. (8), e.g., in diatomic molecules. For consistency we now solve the equations of motion without these assumptions. The magnitude of these corrections is discussed in the Appendix; although they are small the effect is significant enough that these results are not directly comparable with those of Ref. 5. Table VII lists the particle and hole energy levels used in these calculations.

TABLE VII. SCF molecular orbital eigenvalues for C_2H_4 [a]

MO		ϵ_λ	MO		ϵ_m	MO		ϵ_m
1	$1a_{1g}$	-11.2420	9 [b]	$2b_{1u}$	0.0088	21	$3b_{2u}$	0.4351
2	$1b_{3u}$	-11.2405	10	$1b_{2g}$	0.0122	22	$2b_{1g}$	0.4545
3	$2a_{1g}$	- 1.0397	11	$3b_{1u}$	0.0392	23	$5b_{1u}$	0.6580
4	$2b_{3u}$	- 0.7969	12	$2b_{2g}$	0.0456	24	$3b_{1g}$	0.7048
5	$1b_{2u}$	- 0.6565	13	$3b_{2g}$	0.1141	25	$5b_{2g}$	0.7150
6	$3a_{1g}$	- 0.5812	14	$4b_{1u}$	0.1503	26	$6a_{1g}$	0.7325
7	$1b_{1g}$	- 0.5197	15	$4b_{2g}$	0.2124	27	$5b_{3u}$	0.8911
8	$1b_{1u}$	- 0.3731	16	$3b_{3u}$	0.2607	28	$6b_{3u}$	1.1294
			17	$4a_{1g}$	0.2862	29	$7a_{1g}$	1.3051
			18	$2b_{2u}$	0.3838	30	$4b_{2u}$	1.4115
			19	$4b_{3u}$	0.4004	31	$7b_{3u}$	1.4406
			20	$5a_{1g}$	0.4177	32	$4b_{1g}$	1.7326
						33	$8a_{1g}$	23.7659
						34	$8b_{3u}$	24.0592

[a] In a $[(4s2p/2s) + R(3p_z C)]$ basis of contracted Gaussians. This basis gives E_{SCF}: -78.0111 a.u. See Section B.3. for details.

[b] Orbitals 9 - 14 are diffuse functions.

Table VIII shows the excitation energies for the N → T, N → V, and N → R‴ transitions. The N → R‴ transition is the first member of the N → nR‴ Rydberg series according to Wilkinson's assignment.[20] Wilkinson[20] suggested that this R‴ series arose from a $\pi \rightarrow nd\pi_x$ transition. This Rydberg state is of the same symmetry as the V state. As in the results on N_2 and CO we see that the excitation energies obtained by including only 1p - 1h components are larger than the experimental values but when 2p - 2h components are included theory and experiment are in agreement. The excitation energies for the T and V states are 4.1 and 7.9 eV compared with the observed values of 4.6 and 7.6 eV, respectively.[21] The calculated oscillator strength for the vertical transition is 0.40 compared with the experimental total f-value of 0.34 for the N → V band.[22, 23] Our results also show that the π^* orbital of the V state, although somewhat more diffuse than the π^* orbital of the T state, is a valence-like molecular orbital. A valence-like π^* molecular orbital is consistent with most available experimental information on the N → V band. Previous calculations, in both the HF[24] and limited configuration interaction approximation,[25] have given a singlet-state with a diffuse π^* orbital as the lowest state of this symmetry. In the case of the HF calculations it is very probable that in the SCF approximation the lowest state is in fact a Rydberg state. An extensive configuration interaction calculation should give results similar to those of Table VIII, e.g., a valence-like $\pi \rightarrow \pi^*$ state at about 7.8 - 8.0[26] eV. An important consideration in such a calculation would be the inclusion of enough valence-like virtual orbitals to properly describe sigma-pi correlations in addition to diffuse

TABLE VIII. The N→T, N→V, and N→R‴ transitions of C_2H_4[a]

Transition	N[b]	ΔE[c] (1p - 1h)	ΔE[c] (1p - 1h) + (2p - 2h)	ΔE[c] exp.	$\langle\pi^*\|z^2\|\pi^*\rangle$[d]	$f_{calc.}$[e]	f_{obs}
N→T	22	4.8	4.1	4.6	2.7	- -	- -
N→V	22	9.0	7.9	7.6[f]	9.0	0.40	0.34[g]
N→R‴	22	10.4	8.9	9.05[h]	83.3	0.02	0.002 - 0.01[i]

[a]Calculations are all done at approximately the ground state geometry (C–C bond length of 1.35 Å, C–H bond length of 1.07 Å, CH–C–H of 120°).

[b]number of 1p - 1h pairs used in the calculation

[c]in electron volts

[d]the average value of z^2 (perpendicular to the molecular plane) for the π^* orbital (in $(a.u.)^2$)

[e]assuming a Franck-Condon factor of unity for the vertical excitation

[f]maximum in the N→V absorption

[g]total f-value for the transition

[h]This is the N→R‴ transition in Wilkinson's assignment. See text and ref. 20 for discussion.

[i]Preliminary results of Allan Smith and Barney Ellison (Yale University). See text for discussion.

functions, leading to a very large matrix problem.

In Table VIII we also list the excitation energy and oscillator strength for the first $\pi \rightarrow nd\pi_x$ Rydberg state. The calculated excitation energy of 8.9 eV is in good agreement with the value reported by Wilkinson[20] for this Rydberg transition. Wilkinson[20] suggested that the state at 9.05 eV was the first member of a $N \rightarrow R'''$ Rydberg series involving a $\pi \rightarrow nd\pi_x$ transition. This region of the spectrum has recently been remeasured.[22] Our results are in fair agreement with these experimental results and with those of Wilkinson.[20]

D. Potential Energy Curves

1. States of N_2

The electron configuration of the ground state of N_2 is again

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(\pi_u)^4(3\sigma_g)^2.$$

The excitation frequencies and transition moments are determined at six internuclear distances, R = 0.90, 1.00, 1.094 (R_e), 1.20, 1.30, and 1.40 Å, for the following eleven states: B $^3\Pi_g$ and a $^1\Pi_g$ ($3\sigma_g \rightarrow \pi_g$), A $^3\Sigma_u^+$, b' $^1\Sigma_u^+$, B $^3\Sigma_u^-$, a' $^1\Sigma_u^-$, W $^3\Delta_u$, and w $^1\Delta_u$ ($\pi_u \rightarrow \pi_g$), c' $^1\Sigma_u^+$ ($3\sigma_g \rightarrow 3\sigma_u$), C $^3\Pi_u$ and b $^1\Pi_u$ ($2\sigma_u \rightarrow \pi_g$). The principal excitation in each state is in parentheses.

After a Hartree-Fock calculation at each internuclear distance, the equations of motion are first solved in the 1p-1h approximation including all particle-hole pairs of the appropriate symmetry except those of the very low $1\sigma_g$ and $1\sigma_u$ hole levels. The basis set for these calculations contains both contracted valence Gaussian functions, [4s3p], and uncontracted Gaussian functions ($2d_\pi$, $2p\sigma$) at the center of the molecule. This basis set has been described in B.3. We then include the effects of two particle-hole components (2p-2h) on the excitation energies and oscillator strengths.

Table IX lists the excitation energies for the eleven states of N_2 at six internuclear distances. The agreement with experiment is quite good. The excitation frequencies in the (1p-1h) approximation are all larger than the observed values but the inclusion of 2p-2h components leads to a decrease in these excitation energies and excitation frequencies in fairly good agreement with experiment. We do not want to

TABLE IX: Excitation Energies[a]: States of N_2

$X^1\Sigma_g^+$ →		$B\ ^3\Pi_g$		$a\ ^1\Pi_g$		
R(Å)	(1p-1h)	(1p-1h)+ (2p-2h)	Obs.[b]	(1p-1h)	(1p-1h)+ (2p-2h)	Obs.
0.90	12.7	11.0	---	14.6	12.3	---
1.00	10.9	9.0	9.4	12.9	10.3	10.5
1.094[c]	9.6	7.5	8.1	11.5	8.8	9.3
1.20	8.2	5.9	6.8	10.0	7.2	8.0
1.30	7.1	4.8	5.8	8.9	6.1	7.0
1.40	6.3	4.0	4.9	8.0	5.3	6.0
	$A\ ^3\Sigma_u^+$			$B'\ ^3\Sigma_u^-$		
0.90	13.2	12.7	---	15.9	15.1	---
1.00	10.5	9.9	---	13.3	12.4	---
1.094	8.4	7.8	7.8	11.3	10.2	9.7
1.20	6.4	5.7	5.9	9.3	8.1	7.8
1.30	5.1	4.2	4.4	7.9	6.6	6.4
1.40	4.0	3.2	3.2	6.7	5.4	5.3
	$W\ ^3\Delta_u$			$a'\ ^1\Sigma_u^-$		
0.90	14.8	14.3	---	15.9	15.4	---
1.00	12.1	11.5	---	13.3	12.7	---
1.094	10.1	9.4	8.9	11.3	10.6	9.9
1.20	8.1	7.3	7.1	9.3	8.5	8.1
1.30	6.7	5.8	5.6	7.9	6.9	6.6
1.40	5.5	4.7	4.5	6.7	5.8	5.5

TABLE IX (Cont'd)

$W\ ^1\Delta_u$				$b'\ ^1\Sigma_u^+$		
0.9	16.5	15.7	---	19.6	17.9	---
1.0	14.0	13.0	---	18.3	16.6	---
1.094	12.0	11.0	10.3	16.8	15.0	14.4
1.20	10.0	9.0	8.5	15.0	13.2	12.8
1.30	8.6	7.3	7.2	13.1	11.4	11.2
1.40	7.3	6.0	6.0	11.0	9.1	9.7
$c'\ ^1\Sigma_u^+$				$C\ ^3\Pi_u$		
0.90	15.8	12.8	---	14.4	12.5	---
1.00	15.6	12.3	13.0	13.8	11.5	---
1.094	15.5	12.1	12.9	13.3	10.8	11.1
1.20	15.4	12.0	12.6	12.9	10.1	10.6
1.30	15.2	11.6	12.3	12.7	9.6	10.0
1.40	14.9	11.5	---	12.7	9.3	9.3
$b\ ^1\Pi_u$						
0.90	17.7	14.9	---			
1.00	17.6	14.5	---			
1.094	17.4	14.0	13.0			
1.20	17.2	13.4	12.0			
1.30	17.3	12.9	10.7			
1.40	17.5	12.7	9.4			

TABLE IX (Cont'd)

[a] In electron volts.

[b] The experimental results are from W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J., 142, 1227 (1965), and J. Geiger and B. Schroeder, J. Chem. Phys., 50, 7 (1969).

[c] Experimental equilibrium internuclear distance.

make any extensive comparisons between these results and those derived by other methods, since the main purpose is to test the practicality and accuracy of the method and to see how well it does in describing closed-shell systems away from equilibrium geometry. The results of calculations at internuclear distances beyond R = 1.4 become poorer and show that the closed-shell assumption in the theory[6] is beginning to fail at these distances. Some correlation coefficients become as large as 0.3-0.4 at these distances. Fortunately this occurs at distances that are already large for practical spectroscopic interests.

Figures IA to ID are plots of the potential energy curves for these states of N_2 that are derived from these frequencies and the experimental ground state potential energy curve. These derived curves agree quite well with the observed potential energy curves, e.g., the minima are all close to the observed values. Of special interest here are the states labeled $b'\,^1\Sigma_u^+$ and $c'\,^1\Sigma_u^+$. Dressler[30] has shown that the observed $^1\Sigma_u^+$ states in the 12.4-14.3 eV region of the spectrum can be interpreted in terms of "deperturbed" states of a valence type ($b'\,^1\Sigma_u^+$) and a Rydberg type ($c'\,^1\Sigma_u^+$). These "deperturbed" curves correspond to hypothetical electronic states of the same symmetry that are permitted to cross each other.[30] The electrostatic interaction terms between these states is expected to be small, since their electron configurations are very different and hence our calculated potential energy curves should essentially be the deperturbed curves except very close to a crossing point. In Fig. IA, we have drawn our curves for these states as deperturbed curves, and in Fig. IB we preserve the noncrossing rule and show continuous states that assume different electron configurations with

FIGURE I. Potential energy curves for N_2[a]

A. "Deperturbed" representation of the Σ_u^+ states

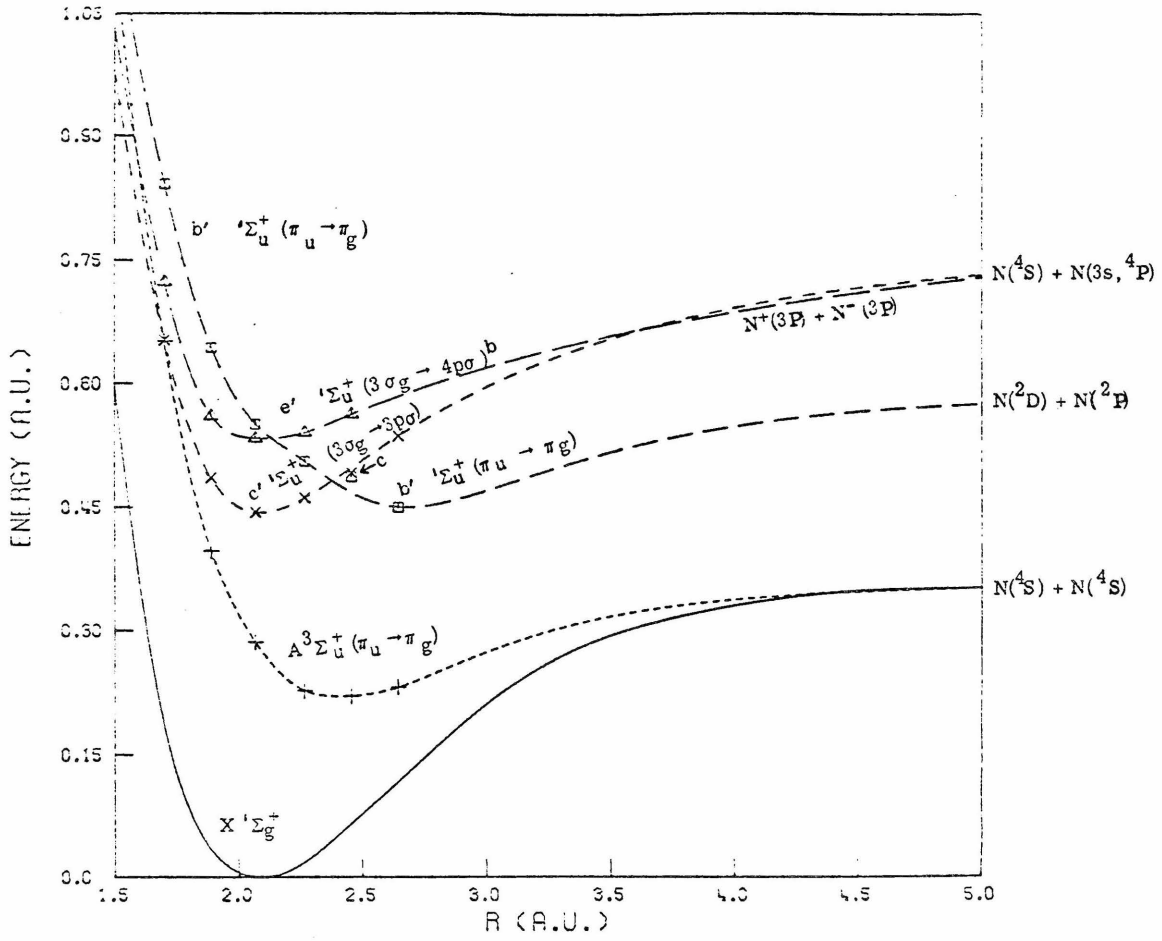


FIGURE I. Potential energy curves for N_2[a]

B. Adiabatic representation of the Σ_u^+ states utilizing the non-crossing rule

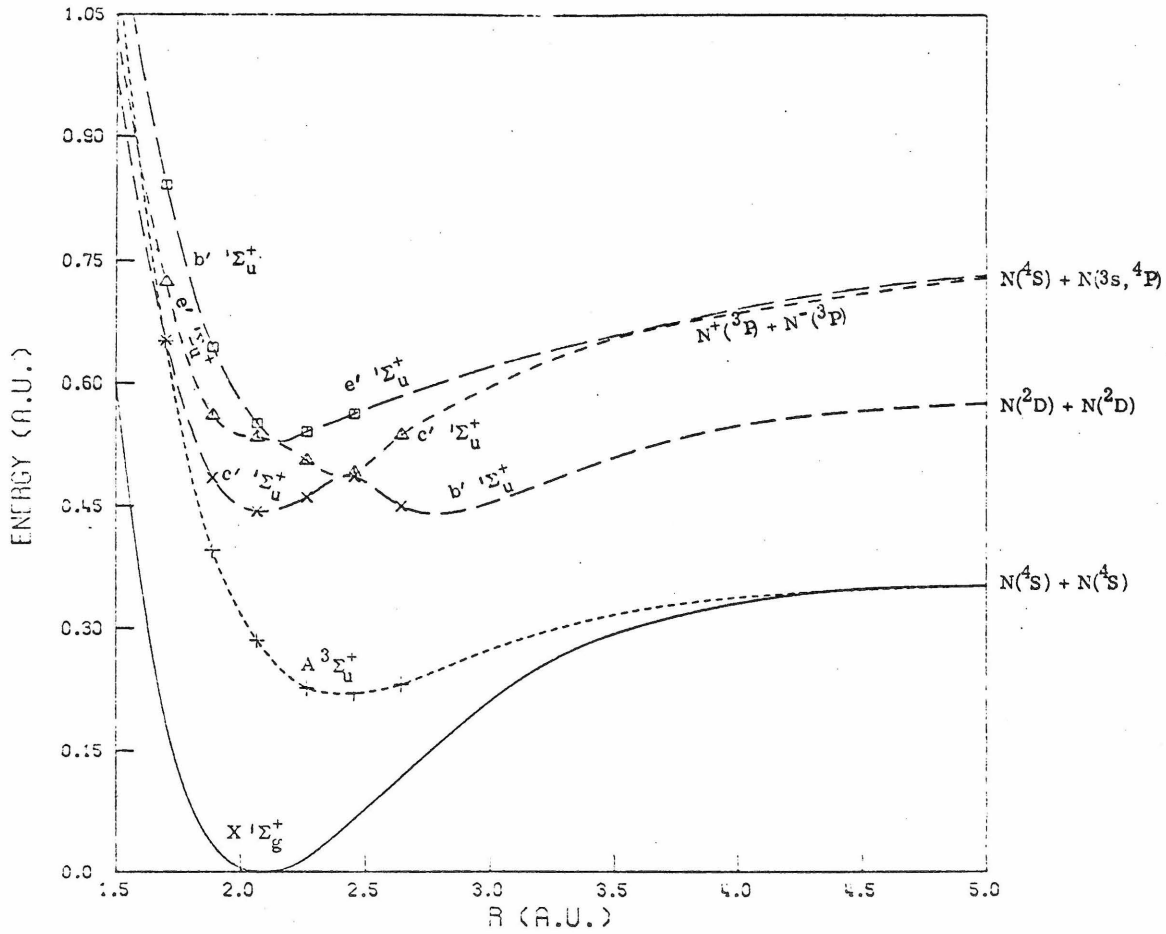


FIGURE I. Potential energy curves for N_2[a]

C. Π_u and Π_g states

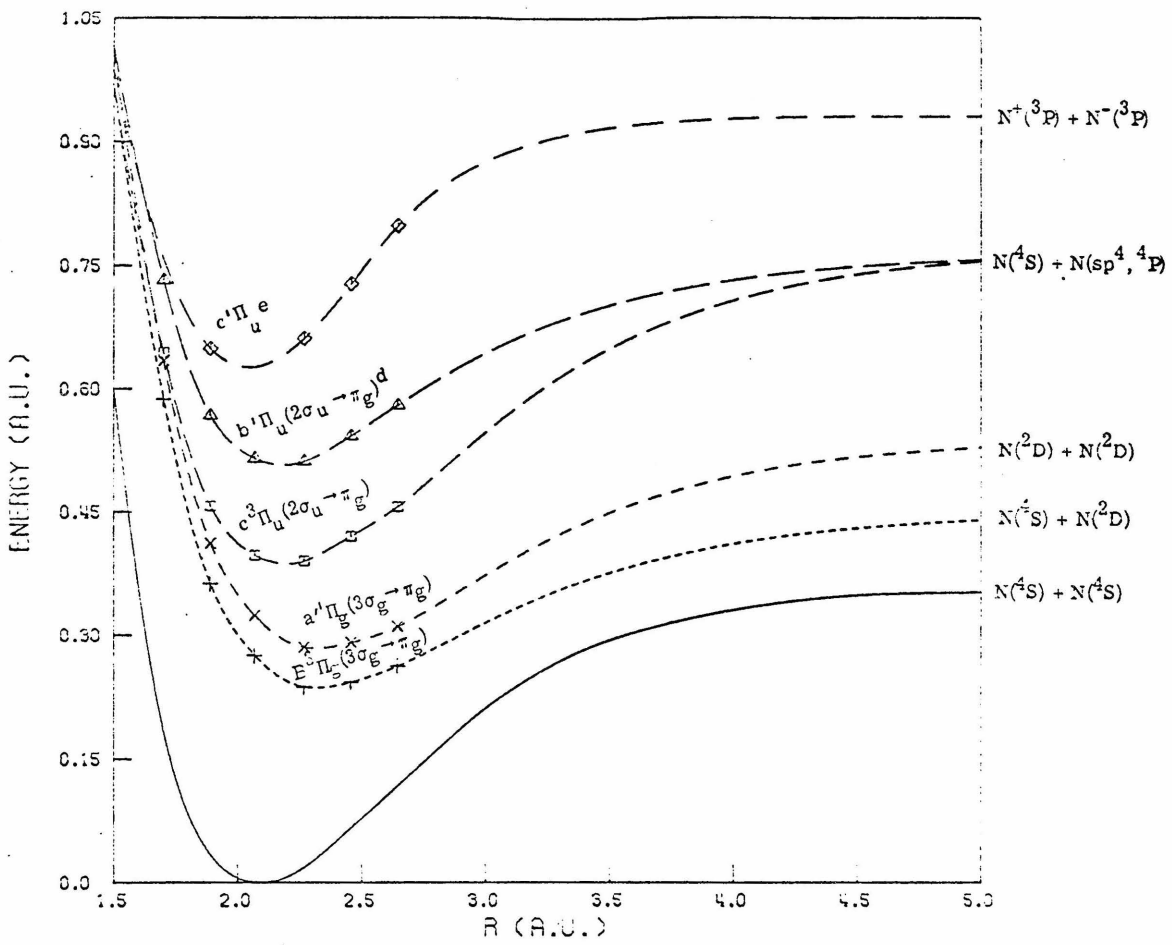


FIGURE I. Potential energy curves for N_2[a]

D. Δ_u and Σ_u^- states (all $\pi_u \rightarrow \pi_g$)

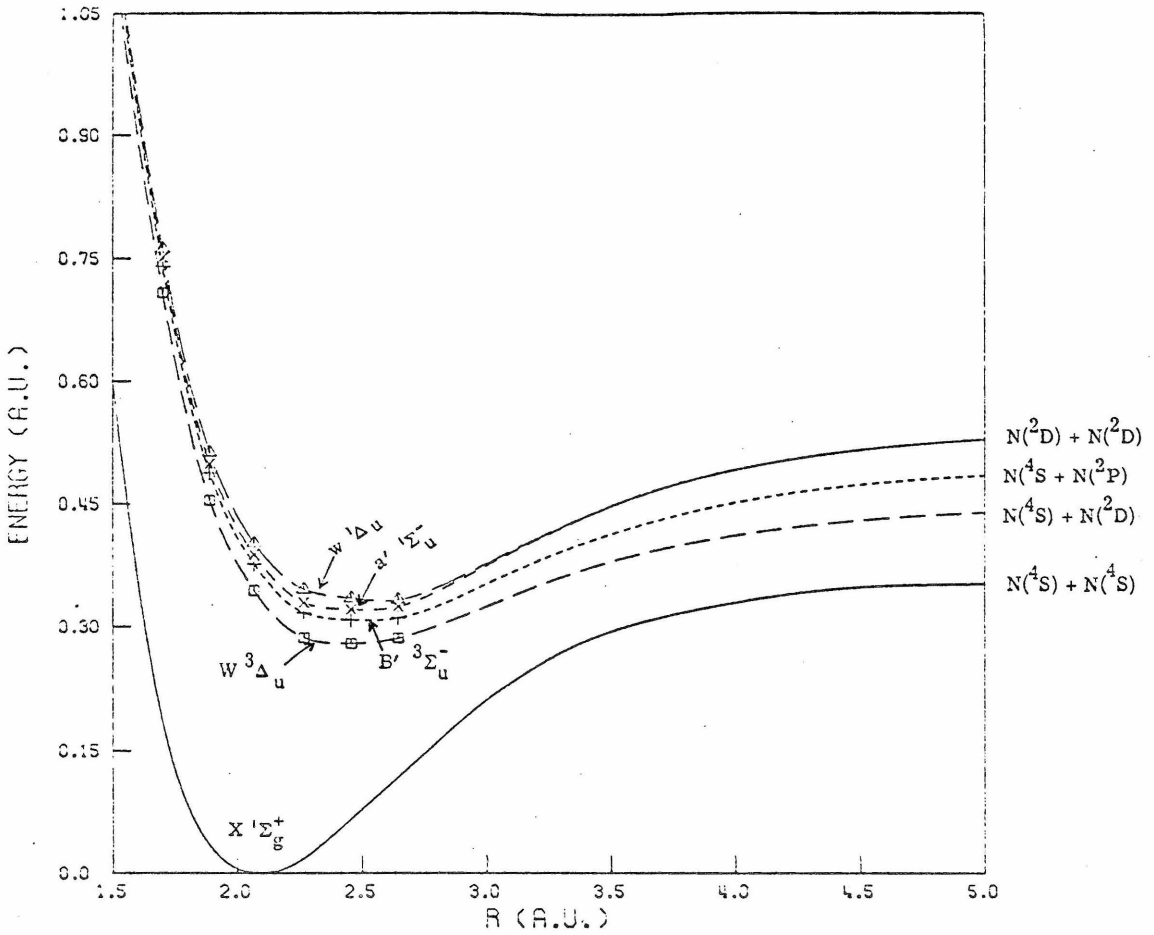


FIGURE I

a. The basis set used is [4s3p] with two diffuse d_π functions and two diffuse p_σ functions at the internuclear center (see Section B.3.) The experimental ground state curve is taken from F. Gilmore, J. Quant. Spectrosc. Radiat. Transfer, 5, 369-390 (1965).

b. This state is poorly described in this basis set. The energy well should be deeper and cross the $b'\,^1\Sigma_u^+$ state at a distance considerably shorter than shown here. Dissociation to ionic nitrogen at 24.5 eV is shown (coulomb repulsion curve).

c. These two points represent strong mixing of the b′ and c′ states near the crossing point and thus do not fall on the deperturbed curves.

d. The $b^1\,\Pi_u$ state is the least well described of the low lying states of N_2 because of the importance of double excitations. At 0.9Å the π_g excited orbital has a mean squared displacement perpendicular to the molecular axis of 13.3 a.u.^{2} and the $b^1\,\Pi_u$ state is essentially a single electronic excitation. In the vertical transition region and beyond, double excitations mix in strongly and the π_g orbital is a typical valence orbital size (from 3.0 to 2.0 a.u.^{2}); the perturbation approach cannot handle the double excitation contribution in excess of 15% adequately and the well is not deep enough.

e. The $c^1\,\Pi_u$ state is probably primarily a $(3\sigma_g \rightarrow 2\pi_u)$ state which is not adequately described in this basis which contains no diffuse π_u

functions. Double excitations are also important and the c state strongly perturbs the b state experimentally (reference 10). The state is included in the plot for completeness although the energy well is not nearly deep enough. Dissociation is shown to $N^+(^3P) + N^-(^3P)$ at 24.5 eV which would be the limit of the doubly excited state. The ($3\sigma_g \rightarrow 2\pi_u$) state dissociates to $N(^4S) + N(3p, ^4D)$ at 21.51 eV.

internuclear distance. Our results agree with the observations of Lefebvre-Brion[31] and Dressler,[30] i.e., the $b'\ ^1\Sigma_u^+$ state is a $\pi_u \rightarrow \pi_g$ intravalence transition with $R_e \cong 2.7$ a.u. and the $c'\ ^1\Sigma_u^+$ a Rydberg $3\sigma_g \rightarrow 3\sigma_u$ transition with $R_e \approx 2.1$ a.u. The deperturbed results give $R_e = 2.73$ a.u. for the $b'\ ^1\Sigma_u^+$ state and $R_e = 2.12$ a.u. for the $c'\ ^1\Sigma_u^+$ state. The observed $^1\Pi_u$ states can also be analyzed by assuming an interaction between a valence $b\ ^1\Pi_u$ state and Rydberg states $c\ ^1\Pi_u$ and $o\ ^1\Pi_u$. Our calculated valence $b\ ^1\Pi_u$ $(2\sigma_u \rightarrow \pi_g)$ has an r_e of about 2.2 a.u., which is smaller than the value of 2.5 a.u. derived by Dressler.[30] The $c\ ^1\Pi_u$ $(3\sigma_g \rightarrow 2\pi_u)$ state is not adequately described in this basis since it does not contain any diffuse π_u components.

Table X gives the electronic oscillator strengths for the $X\ ^1\Sigma_g^+ \rightarrow b\ ^1\Pi_u$, $b'\ ^1\Sigma_u$ and $c'\ ^1\Sigma_u^+$ transitions at several internuclear distances. These oscillator strengths do not contain any Franck-Condon factors. The behavior of the oscillator strength for the $b'\ ^1\Sigma_u^+$ state is very interesting. At smaller internuclear distance, i.e., R = 0.90 and 1.00 Å, the f-value is only about 0.1 but increases to 0.5-0.6 at R = 1.094 and 1.20. The reason for this is that at the smaller distances the π_g orbital begins to acquire some Rydberg character, e.g., the orbital's second moment, $\langle \pi_g | x^2 + y^2 | \pi_g \rangle$, is about 27 $(\text{a.u.})^2$. This reflects the Rydberg-valence mixing of the hypothetical deperturbed states and perhaps the onset of united-atom behavior. At the larger internuclear distances, the state becomes more valence-like, e.g., a π_g orbital second moment of 10 $(\text{a.u.})^2$ at R = 2.3 a.u. We also see that the $X\ ^1\Sigma_g^+ \rightarrow c'\ ^1\Sigma_u^+$ transition has an f-value that becomes very small at R = 2.27 a.u. This is due to the interaction of the $b'\ ^1\Sigma_u^+$ and $c'\ ^1\Sigma_u^+$

states whose "deperturbed" curves cross at R = 2.31 a.u.[30]

TABLE X: Oscillator Strengths for Transitions in N_2.[a]

$X\,^1\Sigma_g^+ \rightarrow b\,^1\Pi_u$			$X\,^1\Sigma_g^+ \rightarrow b'\,^1\Sigma_u^+$	
R(Å)	(1p-1h)	(1p-1h)+ (2p-2h)[b]	(1p-1h)	(1p-1h)+ (2p-2h)[b]
0.90	0.58	0.46	0.13	0.11
1.00	0.62	0.48	0.13	0.11
1.094	0.64	0.46	0.49	0.42
1.20	0.58	0.40	0.59	0.50
1.30	0.58	0.40	0.31	0.26
1.40	0.60	0.36	0.13	0.10
$X\,^1\Sigma_g^+ \rightarrow c'\,^1\Sigma_u^+$				
0.90	0.07	0.05		
1.00	0.09	0.07		
1.094	0.11	0.08		
1.20	0.001[c]	0.001		
1.30	0.12	0.08		
1.40	0.22	0.15		

[a] The electronic oscillator strength $f_{el} = \frac{2}{3}\, G \cdot \Delta E \cdot M$ where M is the dipole transition matrix element and G the degeneracy factor.

[b] These values include the effect of a decrease in the excitation energies in going from the (1p-1h) to (1p-1h) + (2p-2h) approximation and a scaling of the 1p-1h amplitudes due to the inclusion of 2p-2h amplitudes.

[c] Due to an avoided crossing at around R = 1.25 Å. See text for discussion.

2. States of CO

The electron configuration of the ground state of CO is

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2 \quad .$$

We have obtained the excitation frequencies and transition moments at the five internuclear distances, R = 0.98, 1.09, 1.13 (R_e), 1.21, and 1.32 Å, for these states of CO: a $^3\Pi$ and A $^1\Pi$ ($5\sigma \rightarrow 2\pi$), a' $^3\Sigma^+$, e $^3\Sigma^-$, I $^1\Sigma^-$, d $^3\Delta$, D $^1\Delta$, and $^1\Sigma^+$ ($1\pi \rightarrow 2\pi$), B $^1\Sigma^+$ ($5\sigma \rightarrow 3s$), and C $^1\Sigma^+$ ($5\sigma \rightarrow 3p\sigma$). The electron configuration of the principal component of each state is shown in parentheses. The basis set used in these calculations is a [3s2p] contracted valence Gaussian set, plus a single s and pσ on the C and O atoms as used in C.2 with the [4s3p] valence basis, and a diffuse s and pσ function at the center of charge. The calculations at R = 1.09 Å and 1.21 Å were done without the diffuse pσ function. This hardly affects the excitation energies but we will see that the oscillator strengths for the X $^1\Sigma^+ \rightarrow {}^1\Sigma^+$ transitions can depend quite strongly on the composition of the basis.

TableXI shows the excitation energies for nine states at five internuclear distances. The agreement with experiment is quite good. We have also calculated the excitation frequencies at R = 1.43 Å. At this internuclear distance, the predicted excitation energies are all about 0.7-1.0 eV smaller than the observed values. This is primarily due to slight inadequacies in the orbital basis. At this internuclear distance, the correlation coefficients are small enough for the closed-shell assumption to be valid. Of special interest are the results for the I $^1\Sigma^-$

TABLE XI: Excitation Energies[a]: States of CO

$X\ ^1\Sigma^+ \rightarrow$		$a\ ^3\Pi$		$A\ ^1\Pi$		
R(Å)	(1p-1h)	(1p-1h)+ (2p-2h)	Obs.[b]	(1p-1h)	(1p-1h)+ (2p-2h)	Obs.
0.97	8.8	7.4	---	12.2	10.1	---
1.09	7.6	6.5	6.6	11.0	9.1	8.8
1.13	7.2	6.0	6.1	10.3	8.5	8.4
1.21	6.6	5.4	5.6	9.6	7.6	7.7
1.32	5.7	4.4	5.0	8.3	6.1	6.8
	$a'\ ^3\Sigma^+$			$e\ ^3\Sigma^-$		
0.97	13.1	11.2	---	15.6	13.1	---
1.09	10.5	9.1	9.3	12.9	11.0	10.8
1.13	9.5	8.1	8.5	11.9	10.0	9.8
1.21	8.3	6.6	7.0	10.6	8.3	8.2
1.32	6.6	4.5	5.5	8.8	6.0	6.6
	$d\ ^3\Delta$			$I\ ^1\Sigma^-$		
0.97	14.5	12.4	---	15.6	13.3	---
1.09	11.8	10.3	10.1	12.9	11.2	10.9
1.13	10.9	9.3	9.2	11.9	10.2	9.8
1.21	9.6	7.7	7.7	10.6	8.5	8.3
1.32	7.8	5.5	6.1	8.8	6.2	6.7

TABLE XI (Cont'd)

$D\ ^1\Delta$				$B\ ^1\Sigma^{+c}$		
0.97	16.1	13.5	---	12.3	10.3	10.6[d]
1.09	13.4	11.5	---	12.9[e]	11.0	10.8
1.13	12.5	10.4	10.5	12.8	10.9	10.8
1.21	11.1	8.7	8.4	13.1[e]	11.0	10.8
1.32	9.3	6.3	6.8	12.9	10.5	10.8[d]

$C\ ^1\Sigma^{+c}$			
0.97	13.0	10.9	---
1.09	13.5[e]	11.4	---
1.13	13.5	11.3	11.4
1.21	13.8[e]	11.5	---
1.32	14.9	12.4	---

[a] In electron volts. The experimental R_e is 1.13 Å.

[b] The experimental results are from G. Herzberg, T. Hugo, S. Tilford, and J. Simmons, Can. J. Phys., 48, 3004 (1970) and V. Meyer, A. Skerbele, and E. Lassettre, J. Chem. Phys., 43, 805 (1965).

[c] The calculated excitation energies to the $b\ ^3\Sigma^+$ and $c\ ^3\Sigma^+$ states, the triplet states corresponding to the $B\ ^1\Sigma^+$ and $C\ ^1\Sigma^+$ states, are 10.5 and 11.2 eV at R = 1.13 Å compared to the observed values of 10.4 and 11.6 eV, respectively.

[d] Estimated from a plot of the measured values at R = 1.09, 1.13, and 1.21 Å.

TABLE XI (Cont'd)

[e] The excitation energies at this point were calculated without the diffuse pσ function at the center of charge. See text for discussion.

state, which are all within 2-7% of the observed values reported by Herzberg et al.[32] These results are quite different from those deduced by Krupenie,[33] e.g., the excitation energies at R = 0.97 Å and 1.09 Å are given as 7.8 eV and 9.1 eV, respectively, in Ref. 33. Our results therefore suggest that the experimental potential energy curve of Ref. 32 is the correct one for R < 1.09 Å.

As in the results for N_2, the calculated excitation energies are used with the experimental potential energy curve for the ground state to construct potential energy curves for the various states of CO in Figs. IIA to IID. These curves all agree well with experiment. Of special interest are the curves for the $^1\Sigma^+$ states. Figure IA shows these potential curves for four $^1\Sigma^+$ states, i.e., B $^1\Sigma^+$ ($5\sigma \rightarrow 3s$), C $^1\Sigma^+$ ($5\sigma \rightarrow 3p\sigma$), $^1\Sigma^+$ (R), and, at a few points, $^1\Sigma^+$ ($1\pi \rightarrow 2\pi$), a valence state. In this Figure we draw these curves to correspond to approximate "deperturbed" curves that are therefore shown as crossing one another.[30] The $^1\Sigma^+$ (R) is a Rydberg-like state that cannot be adequately described in the present orbital basis, especially at larger internuclear distances where it cannot retain its Rydberg character in this basis. The curve for this state is therefore just an approximate one. This calculation also predicts a $^1\Sigma^+$ state that is valence-like with $1\pi \rightarrow 2\pi$ as the principal component of the excitation. This state may play a role in the Σ^+ spectrum of CO in this region, similar to that of the b' $^1\Sigma_u^+$ state of N_2. The predissociation of the v' = 2 level of the B $^1\Sigma^+$ state is probably due to the a' $^3\Sigma^+$ to some extent,[34] but the location of this $^1\Sigma^+$ ($1\pi \rightarrow 2\pi$) state relative to the B $^1\Sigma^+$ suggests that some predissociation may take

FIGURE II. Potential energy curves for CO[a]

A. "Deperturbed" representation of the Σ^+ states

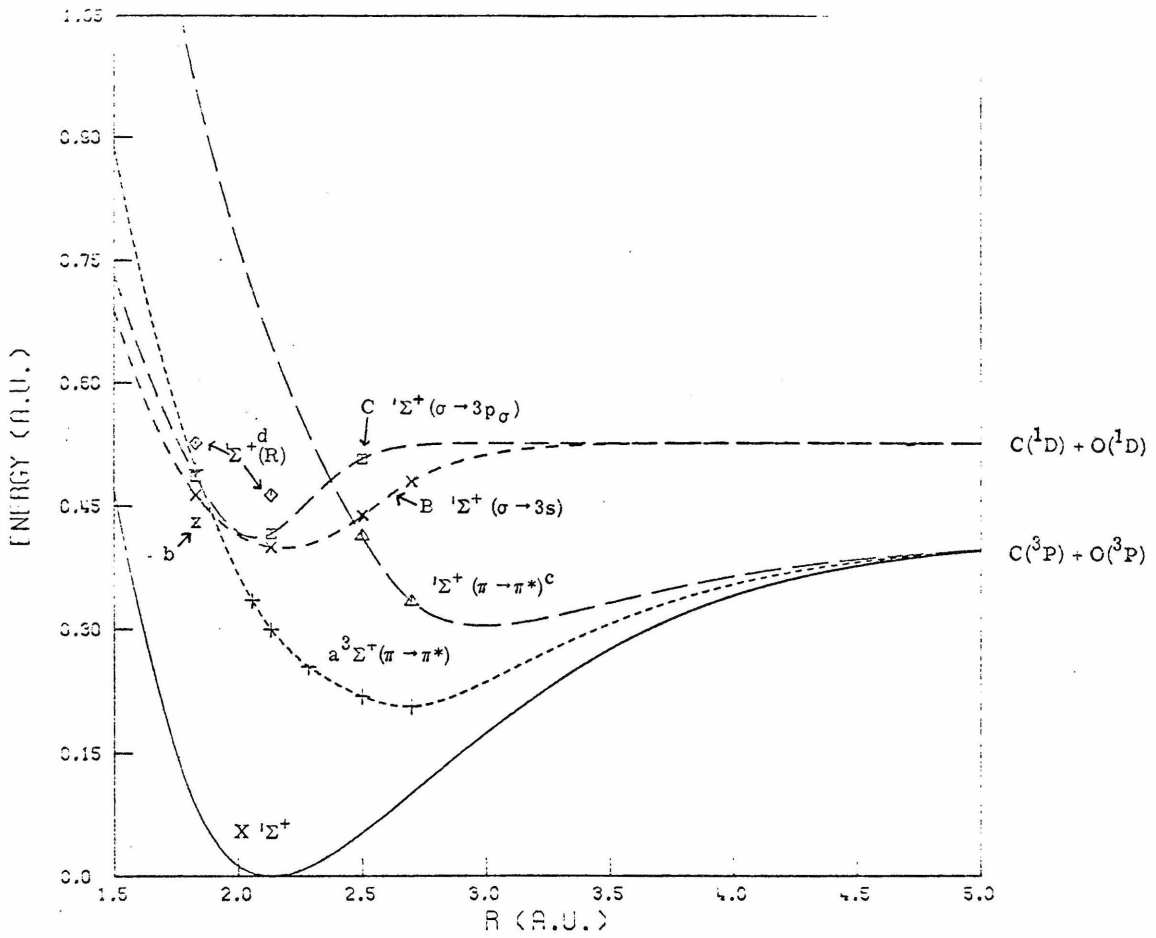


FIGURE II. Potential energy curves for CO[a]

B. Adiabatic representation of the Σ^+ states

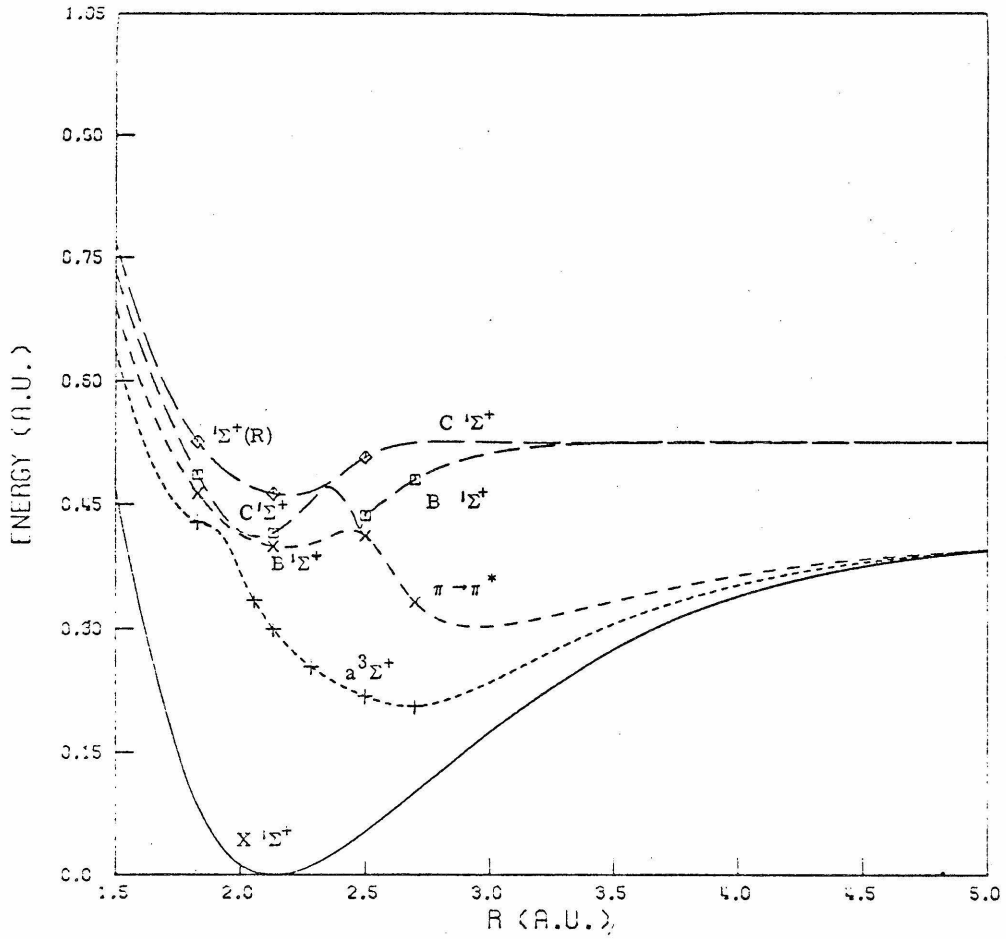


FIGURE II. Potential energy curves for CO[a]

C. II states

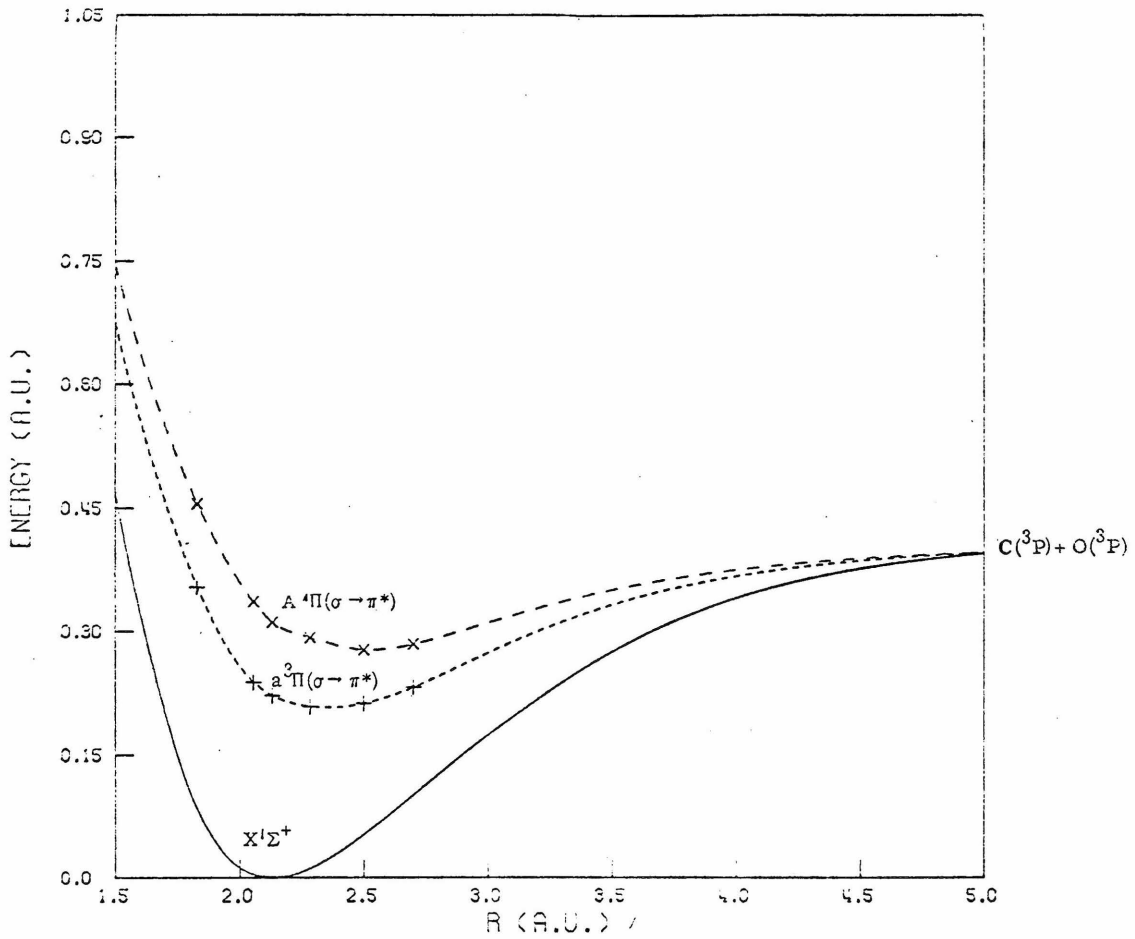


FIGURE II. Potential energy curves for CO[a]

D. Δ and Σ^- states (all $\pi \rightarrow \pi^*$)

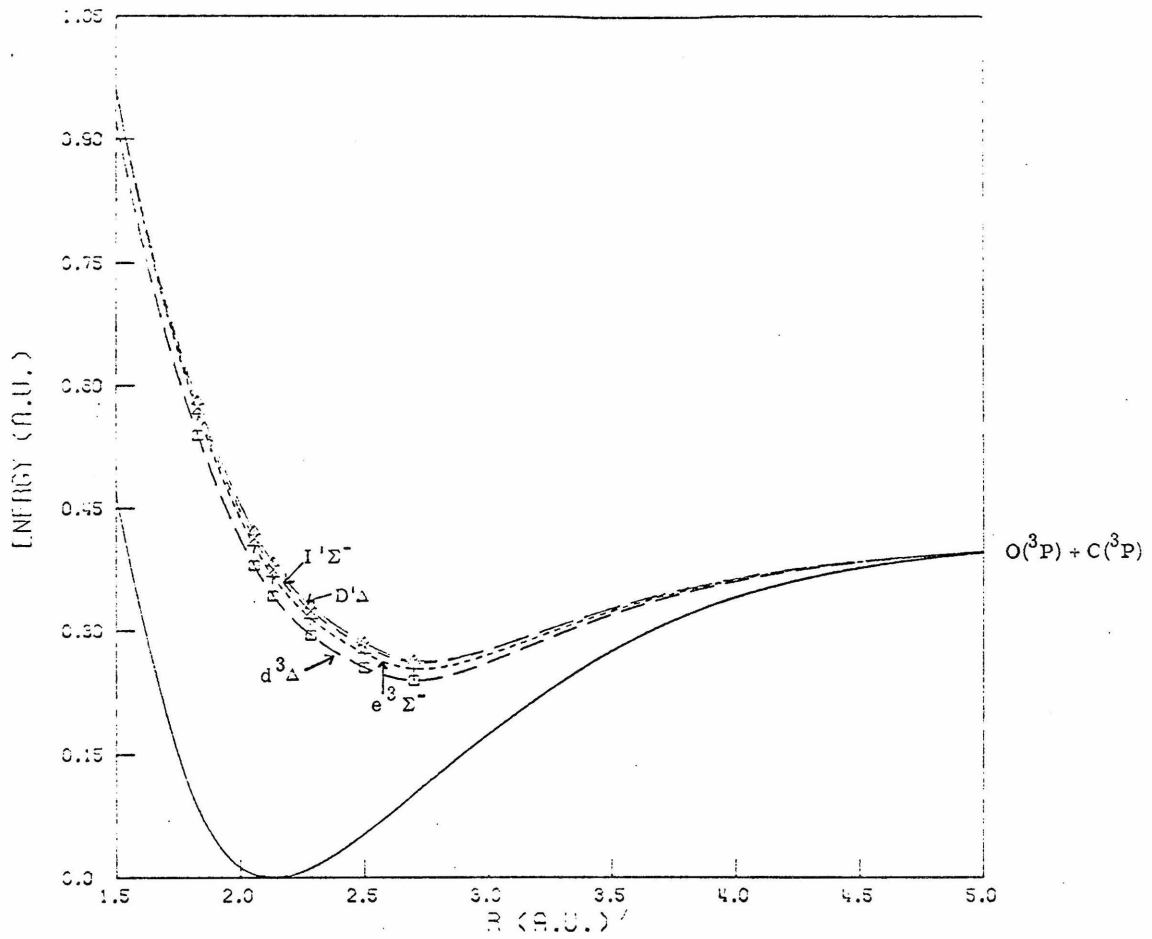


FIGURE II

a. The basis set used is [4s, $2p_\pi$ $3p_\sigma$] ([3s2p] valence basis contracted from a (7s3p) primitive basis plus 3s and 3pσ functions on carbon (ζ = .036, .030) and oxygen (ζ = .048, .040)) with an additional 4s (ζ = .01) and $4p_\sigma$ (ζ = .0085) at the center of charge. As mentioned in the text the points at 1.09Å and 1.21Å were computed without the $4p_\sigma$ function; this function only affects the Σ^+ Rydberg states (lowering the $B^1\Sigma^+$ and $C^1\Sigma^+$ states by 0.1 and 0.2 eV respectively) so that all five distances are plotted except for these states for which three points are used. The $X^1\Sigma^+$ ground state curve is taken from the experimental data of Krupenie, Natl. Std. Ref. Data Ser., Natl. Bur. Std. (U.S.) 5, (1966).

b. This point represents a $^3\Sigma^+$ ($\sigma \rightarrow 3s$) Rydberg state which is the lowest state of this symmetry at small internuclear distances. For all the other distances plotted the $a'\,^3\Sigma^+$ ($\pi \rightarrow \pi^*$) state is at lower energy.

c. The valence $\pi \rightarrow \pi^*$ state only appears in the low energy region at large internuclear distances. This is analogous to the $b'\,^1\Sigma_u^+$ state of N_2 and may cause predissociation of the $B\,^1\Sigma^+$ state (see text).

d. These points represent a Rydberg state (probably the next member of the $\sigma \rightarrow ns$ series which has erroneously been assigned as $F^1\Pi$ experimentally [T. Betts and V. McKoy, J. Chem. Phys. 54, 113 (1971)] that is inadequately described in this basis. At larger distances this

combination of orbitals produces a spurious valence state which may have altered the other $^1\Sigma^+$ curves; these effects would be eliminated by adding more diffuse σ functions to the basis set.

place through this mechanism. The variation of the lifetime with vibrational quantum number[35] for $v' = 0$ and 1 vibrational levels of the B $^1\Sigma^+$ state may also be due to perturbations between these two states. In Fig. IIB we preserve the noncrossing rule and show continuous potential energy curves for these states. Our calculated excitation energies for the b $^3\Sigma^+$ and c $^3\Sigma^+$ states are 10.5 eV and 11.2 eV at R_e of the ground state. These values agree well with experiment, i.e., 10.4 eV and 11.6 eV, respectively, and are not listed in TableXI.

In TableXII we give the oscillator strengths for the X $^1\Sigma^+ \rightarrow$ A $^1\Pi$, B $^1\Sigma^+$, and C $^1\Sigma^+$ transitions at the various internuclear distances. From the electron energy loss spectra, Lassettre[14] has obtained the dependence of the electronic transition moment on internuclear distance for the X $^1\Sigma^+ \rightarrow$ A $^1\Pi$ (Fourth Positive) band. It is now known that it is necessary to include this variation of the transition moment with R to remove the discrepancy that existed between total f-values derived from lifetime data and electron energy loss spectra.[15] In Table XIII we show our calculated values of the transition moment, $\langle X\ ^1\Sigma^+ | \sum_i \underset{\sim}{r}_i | A\ ^1\Pi \rangle$, at five internuclear distances. In the second column of this Table, we also list the experimental values[14] for M(R) at $R \approx 1.09$ Å and 1.13 Å, which are the two values that lie in our range of R. The agreement between the calculated transition moment and the experimental values is good. **Figure III** shows a plot of M(R) along with a plot of Lassettre's data.

The calculated f-values for the X $^1\Sigma^+ \rightarrow$ B $^1\Sigma^+$ and C $^1\Sigma^+$ transitions can be sensitive to the basis set used in the calculation. This is due to the fact that they are Rydberg-like states. For example, the

TABLE XII: Oscillator Strengths for Transitions in CO.[a]

$X\ ^1\Sigma^+ \rightarrow A\ ^1\Pi$			$X\ ^1\Sigma^+ \rightarrow B\ ^1\Sigma^+$ [c]	
R(Å)	(1p-1h)	(1p-1h)+ (2p-2h)[b]	(1p-1h)	(1p-1h)+ (2p-2h)
0.97	0.34	0.28	0.03	0.03
1.09	0.22	0.18	---	---
1.13	0.18	0.14	0.04	0.03
1.21	0.14	0.10	---	---
1.32	0.06	0.04	0.06	0.04
$X\ ^1\Sigma^+ \rightarrow C\ ^1\Sigma^+$ [c]				
0.97	0.04	0.03		
1.09	---	---		
1.13	0.06	0.04		
1.21	---	---		
1.32	0.06	0.05		

[a] The electronic oscillator strength $f_{el} = \frac{2}{3} \cdot G \cdot \Delta E \cdot M^2$ where M is the dipole transition matrix element and G the degeneracy factor.

[b] See footnote b of Table II.

[c] The oscillator strengths for the $B\ ^1\Sigma^+$ and $C\ ^1\Sigma^+$ states are strongly affected by the diffuse components of the orbital basis. We only report values for the most complete and balanced basis. See text for discussion.

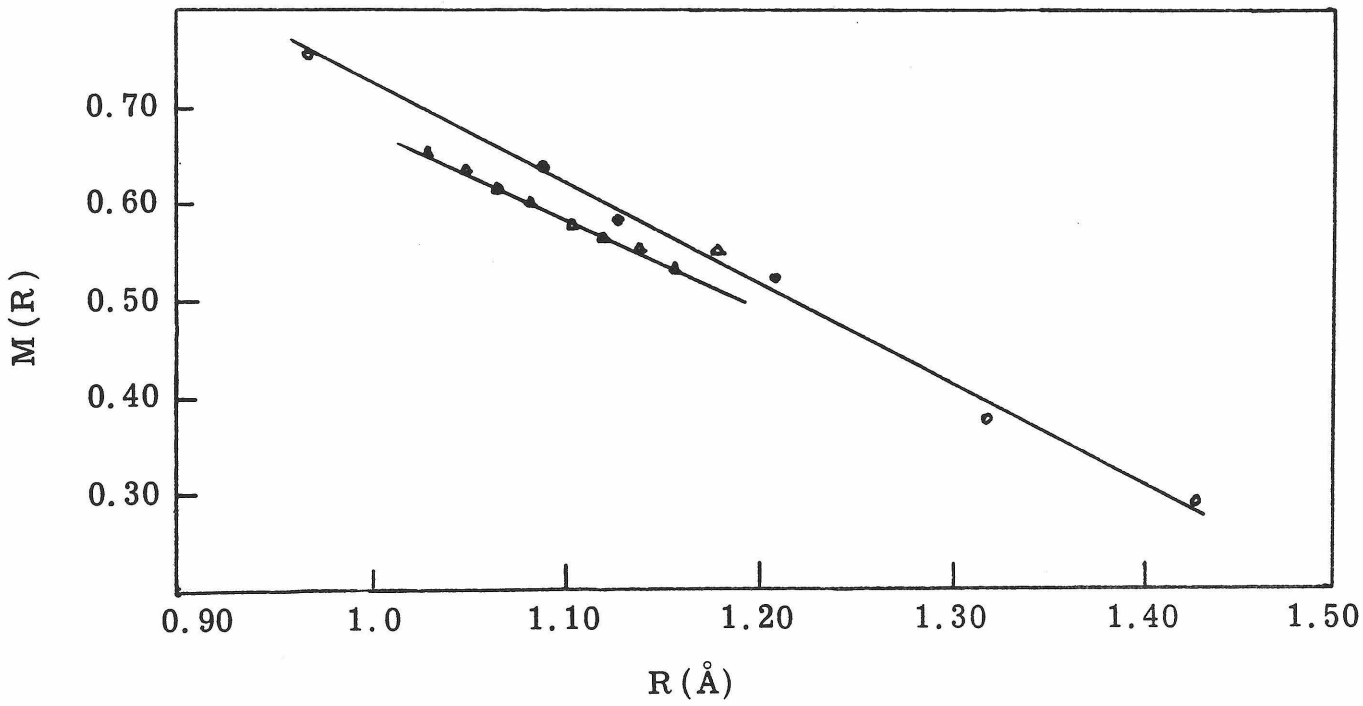
TABLE XIII. Dependence of the transition moment on internuclear distance in the Fourth Positive band of CO.

R (Å)	M(R)[a]	$M_{obs.}$[b]
0.97	0.753	
1.09	0.636	0.59
1.13	0.580	0.56
1.21	0.518	
1.32	0.365	

[a] In atomic units. These values of M(R) are derived from the (1p-1h) + (2p-2h) values of f in Table XII.

[b] These two values of Ref.30 lie within our range of R. See Fig. for a plot of the other data.

FIGURE III. Transition moment, M(R), vs. internuclear distance for the fourth positive bands of CO[a]



[a] Circles are the calculated points and the triangles are the experimental values of ref. 14.

f-values obtained in the more complete calculation of C.2. are 0.05 and 0.12 for the B and C states, respectively, at R = 1.13 Å. There we used a [5s4pσ, 3pπ] basis. This f-value of 0.12 for the X → C transition, although in better agreement with the observed value of 0.16, would probably be lowered if more diffuse Rydberg-like functions are added to the basis.

3. States of Ethylene

Tables XIV-XVI show the results of calculations on the $N \rightarrow T\,(^3B_{3u})$, $N \rightarrow V\,(^1B_{3u})$, and $N \rightarrow R'''\,(^1B_{3u})$ transitions in ethylene. The T and V states are the triplet and singlet $\pi \rightarrow \pi^*$ states and R''' is the first member of $\pi \rightarrow nd\pi_g$ Rydberg series. This Rydberg state is of the same symmetry as the V state. In C.3. results are given of calculations on these same states with a large basis, i.e., [4s3p/2s] + R($3p_z$) Gaussian basis, but only at the ground state equilibrium geometry. These new results show the dependence of the excitation frequencies and oscillator strengths of these transitions on internuclear geometry.

Table XIV gives the excitation frequencies of these transitions at six C-C internuclear distances for the planar molecule. The results at R = 1.35, R_e of the ground state, can be compared with the experimental vertical excitation energies of 4.6, 7.6, and 9.0 eV, respectively.[36] The results in C.3. are in better agreement with experiment especially for the $N \rightarrow R'''$ transition where we obtained an excitation frequency of 8.9 eV. However the excitation energies in this basis for this transition should give a reasonable potential energy curve but shifted to higher energies. One of our purposes is to obtain potential energy

TABLE XIV. Excitation energies: states of C_2H_4 as a function of C-C bond distance.[a]

N →	T ($^3B_{3u}$)[b]		V ($^1B_{3u}$)		R‴ ($^1B_{3u}$)[d]	
R_{C-C}(Å)	(1p-1h)	(1p-1h) + (2p-2h)	(1p-1h)	(1p-1h) + (2p-2h)	(1p-1h)	(1p-1h) + (2p-2h)
1.24	6.1	5.5	10.9	9.8	12.7	11.1
1.35[c]	4.8	4.0	9.7	8.2	12.0	10.6
1.46	3.7	3.0	8.6	7.5	11.4	10.1
1.57	2.9	2.1	7.6	6.3	11.1	9.8
1.69	2.1	1.3	6.5	5.0	10.8	9.5
1.80	1.5	0.5	5.5	3.8	10.5	9.3

[a] Calculations are all done at a C-H bond length of 1.07 Å and a CH-CH bond angle of 120° and in the planar geometry.

[b] Excitation energies in eV's.

[c] R_e of the ground state. See C.3. for a comparison of the calculated and experimental results at R_e.

[d] The first member of the Rydberg series of the same symmetry as the V state.

TABLE XV. Oscillator strengths for the N → V transition at several C-C distances.[a]

R(Å)	(1p-1h)[b]	(1p-1h) + (2p-2h)
1.24	0.44	0.34
1.35[c]	0.40	0.33
1.46	0.33	0.28
1.57	0.24	0.20
1.69	0.15	0.11
1.80	0.10	0.07

[a] For planar ethylene with a C-H bond length of 1.07 Å and a CH-CH bond angle of 120°.

[b] $f_{el} = \frac{2}{3} \cdot \Delta E \cdot M^2$ where M is the transition moment. No Franck-Condon factors are included in this table.

[c] R_e of the ground state. See C.3. for a comparison with experimental results.

TABLE XVI. Excitation energies: states of C_2H_4 at several torsional angles.[a]

N →	$T(^3B_{3u})^c$		$V(^1B_{3u})^c$		$R'''(^1B_{3u})$	
θ[b]	(1p-1h)	(1p-1h) + (2p-2h)	(1p-1h)	(1p-1h) + (2p-2h)	(1p-1h)	(1p-1h) + (2p-2h)
0°	4.8	4.0	9.7	8.2	12.0	10.6
30°	3.9	3.4	8.0	7.1	9.7	8.4
45°	2.9	2.3	6.6	5.7	9.2	7.9

[a] With a C-H bond length of 1.07 Å and a CH-CH bond angle of 120° and R_{C-C} = 1.35 Å.

[b] The calculations at 30° and 45° were done in a [3s2p/1s] contracted valence plus two p_y and p_z diffuse Gaussian basis.

[c] See text for a comparison with available experimental data.

curves for planar ethylene in the T, V, and R''' states. To obtain these curves, we assume a Morse curve for the C-C stretching in the ground state with R_e = 1.35 Å, ω = 1600 cm^{-1}, and $D_e \approx$ 146 kcal/mole. From this ground state potential energy curve and the excitation frequencies of TableXIV we obtain the potential energy curves for the T, V, and R states shown in Fig.IVA. The V state is drawn with a dissociation limit of 8 eV.[37] These curves give C-C bond lengths in these states in agreement with the suggested experimental values.[36] The curves are approximate but reasonable changes in the dissociation limits will not change these estimates drastically. The T state has an R_e of about 1.55 Å while the V state has a minimum around 1.7-1.8 Å. Mulliken[12-36] suggests values of 1.58 Å and 1.8 Å for R_e of the T and V states, respectively. The potential energy curve for the R''' state has a minimum at around R = 1.42 Å, which agrees well with the value of 1.41 Å observed for most Rydberg states of ethylene.[20] The b_{2g} (or π^*) orbital has a second moment in the direction perpendicular to the molecular plane, i.e., $\langle \pi^* | z^2 | \pi^* \rangle$ of about 6 $(a.u.)^2$ and 66 $(a.u.)^2$ in the V and R''' states, respectively. The N → V transition is clearly an intravalence transition. Finally, we list the oscillator strengths for the N → V transition at several internuclear distances in Table XV. The f-value of 0.33 for the vertical transition at the ground state R_e is close to the suggested total f-value of N → V band. The basis set used in these calculations is not adequate to describe the f-value of the N → R''' transition at larger C-C distances.

Table XVI lists excitation energies at torsional angles of 30° and 45° for N → T, V, and R''' transitions. In these calculations the C-C

FIGURE IV. Potential energy curves for C_2H_4[a]

A. B_{3u} states as a function of C-C stretch[b]

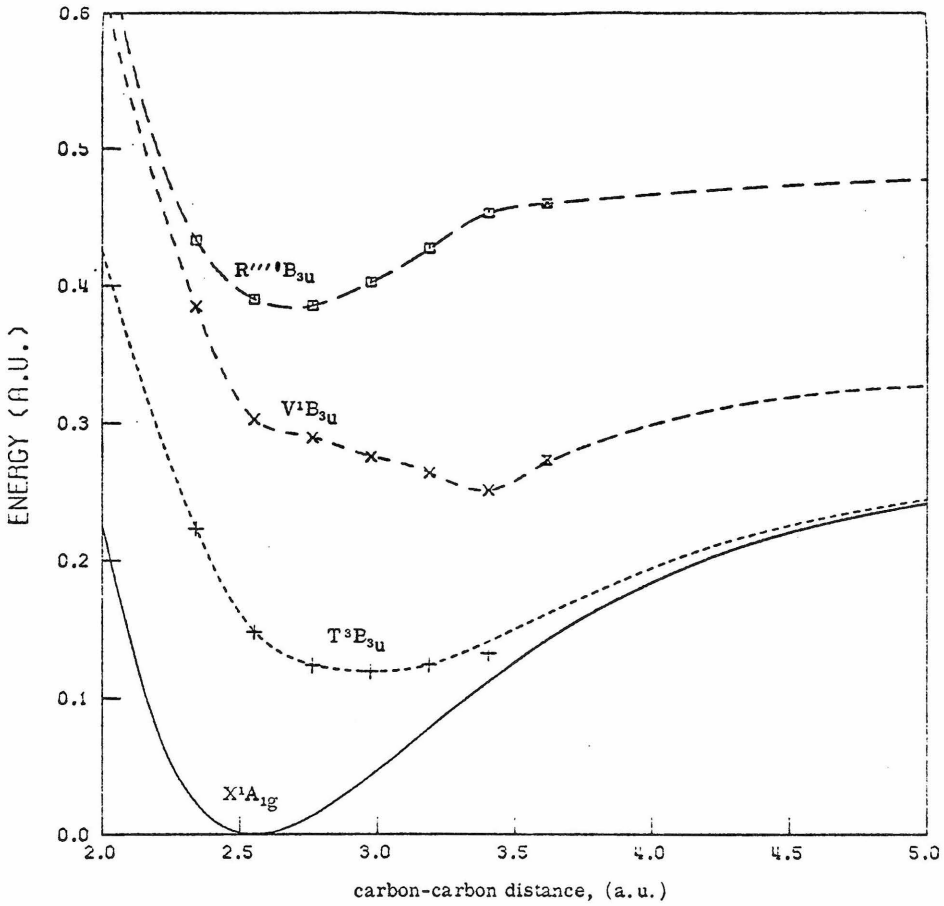


FIGURE IV. Potential energy curves for C_2H_4[a]

B. B_{3u} states as a function of twisting about the C-C bond[c]

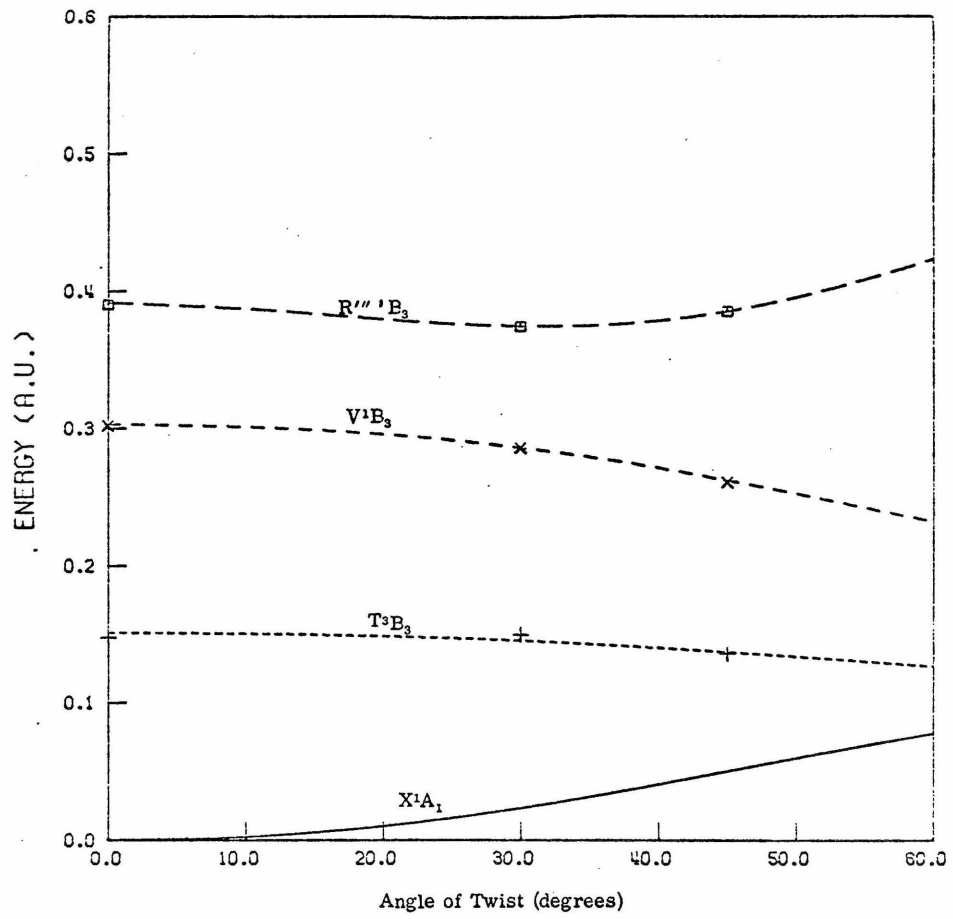


FIGURE IV

a. The basis set employed is [3s2p] + R($2p_\pi$ C) utilizing a contracted (7s3p) primitive set (reference 29) with two diffuse p_z functions on each carbon (ζ = .03, .01) and, in the case of twisted ethylene, identical p_y functions also.

b. The ground state curve for stretching is generated by the Morse function $\Delta E = 7.3\ (1-e^{-2.3(R-1.35)})^2$ while R is in angstroms and ΔE is in electron volts. The points at 1.80 Å (3.4 a.u.) are inaccurate because the closed shell gound state approximation is beginning to fail at this distance. The modified symbols at 1.91 Å (3.6 a.u.) indicate that the ground state correlation coefficients are the perturbation theory estimates since the equations-of-motion are no longer self-consistent in the (1p-1h) approximation.

c. The ground state curve for twisting is taken as $\Delta E = 2.3 \sin^2\ominus + 1.3 \sin^4\ominus - 0.8 \sin^6\ominus$ where ΔE is in eV. This fits the CI data of Kaldor and Shavit, J. Chem. Phys. 48, 191 (1968) up to about 45° and matches the experimental barrier of 2.8 eV (B.S. Rabinovitch and F.S. Looney, J. Chem. Phys. 23, 315 (1955)).

distance is kept at 1.35 Å. Calculations at 60° showed that some ground state correlation coefficients become large and hence we could not make the closed-shell assumption for the ground state wavefunction. An open-shell version of the equations-of-motion method would have to be used. In Fig. IV B potential curves are plotted for these states from the calculated excitation energies and the suggested potential energy curve for torsion in the ground state. To compare the calculated frequencies with experiment, we assume the potential energy curves of the V and T states given in Ref. 36 but shifted so as to give the observed excitation energies of 7.6 and 4.6 eV at $\theta = 0°$ for the V and T states, respectively. The calculated frequencies agree well with these suggested experimental results. At twisting angles $\theta = 0°$, 30°, and 45°, the calculated values for the N → T transition are 4.0, 3.4, and 2.3 eV, respectively, and the available experimental data suggest[36] values of 4.6, 3.2, and 1.9 eV. For the N → V transition the values are 8.2, 7.1, and 5.7 eV at $\theta = 0°$, 30°, and 45° compared with the probable experimental values of 7.6, 6.4, and 5.0 eV, respectively. The curve for the R‴ state shows a minimum at a torsional angle of about 30° in agreement with the observed minima at an angle of 25° in other Rydberg states and the $^3B_{1u}$ positive ion of ethylene.[36] The oscillator strength for the N → V transition decreases from a value of 0.33 at $\theta = 0°$ to 0.08 at 45°. From the orbital second moments, the electron density is obviously becoming less diffuse in both the V and R‴ states as the molecule is twisted.

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II. Applicability of SCF Theory to Some Open-Shell States of CO, N_2, and O_2

A. Introduction

The Hartree-Fock model provides a useful description of the electronic structure of atoms and molecules. For closed-shell systems, the Hartree-Fock (HF) wavefunction is an antisymmetrized product of orthogonal spin orbitals which satisfy the pseudo-eigenvalue equation,

$$F\varphi_i = \epsilon_i \varphi_i \ , \tag{1}$$

where

$$F = h + \sum_{i=1}^{N} (2J_i - K_i) . \tag{2}$$

h is the nuclear field plus kinetic energy operator for each electron, and J_i and K_i are the Coulomb and exchange operators associated with the doubly-occupied orbital φ_i. For open-shell systems, the total wavefunction is, in general, a sum of Slater determinants. In these cases there are two complicating features which do not occur in the closed shell equations, Eqs. (1) and (2): (i) the off-diagonal Lagrange multipliers ϵ_{ij} cannot, in general, be eliminated by an arbitrary unitary transformation and will therefore appear in Eq. (1), and (ii) it is not always possible to express the HF operator in terms of Coulomb and exchange operators only. For some types of open-shell configurations the first difficulty can be handled by Roothaan's coupling operators[1] but the recently proposed Orthogonality Constrained Basis Set Expansion (OCBSE) method is

much more convenient and general.[2] The second difficulty arises in systems with two or more open shells in which, in addition to the usual terms in the expression for the total energy, we have a term representing the interaction between two open shells. In the notation of Ref. 1, this is the term

$$I = 2\,ff' \sum_{mm'} I_{mm'} \quad , \tag{3}$$

where m and m′ refer to orbitals in the first and second open shells, respectively, and f and f′ are the usual fractional occupations of the open shells. For example, in the B $^3\Sigma_u^-$ state of oxygen with the configuration $\pi_u^3\pi_g^3$, I, Eq. (3) would be

$$I(^3\Sigma_u^-) = 9\,J(\pi_u^+, \pi_g^+) - 3\,K(\pi_u^+, \pi_g^-) - K(\pi_u^+, \pi_g^+)$$

$$- \langle \pi_u^-(1)\pi_g^+(2) | \pi_u^+(1)\pi_g^-(2) \rangle \quad , \tag{4a}$$

where

$$\langle \pi_u^-(1)\pi_g^+(2) | \pi_u^+(1)\pi_g^-(2) \rangle = \int \pi_u^{-*}(1)\pi_g^{+*}(2)\frac{1}{r_{12}}\pi_u^+(1)\pi_g^-(2)d\tau \; . \tag{4b}$$

Upon variation of the total energy, an integral such as (4b) leads to an operator which cannot be expressed as a sum of Coulomb and exchange operators. All eight Σ states arising from the configurations $\pi_u^3\pi_g$ and $\pi_u^3\pi_g^3$ contain such integrals. The presence of such terms in the HF Hamiltonian matrix is a complicating factor in trying to set up a general computer program to treat open-shell states.

In this paper we show that by working with the real functions π_x and π_y instead of π^+ and π^-, we can write the energy expressions for Σ states of the configurations $(\pi_u)^3(\pi_g)$, $(\pi_u)^3(\pi_g)^3$ and $(1\pi)^3(2\pi)$ for diatomic molecules in terms of Coulomb and exchange integrals only. This means that the HF operator now contains only the Coulomb and exchange operators J_i and K_i. This is an immediately useful result for it allows us to solve correctly for the SCF solutions of the $^1\Sigma_u^+$, $^3\Sigma_u^+$, $^1\Sigma_u^-$, and $^3\Sigma_u^-$ states of N_2 and O_2 and the analogous states in CO. Many of these states are of spectroscopic interest, e.g., the B $^3\Sigma_u^-$ state of O_2 and the b' $^1\Sigma_u^+$ of N_2. These calculations can be done using existing open-shell SCF programs. In the next section we discuss the algebraic identities which are used to express the interaction terms $I_{mm'}$ in terms of the J and K integrals. We also list the coefficients needed to set up the new HF matrices.

In Secs. C and D we give the SCF results for most of the low-lying excited states of N_2, O_2, and CO. For N_2 and CO, these calculations are all done at the ground state geometry, but for O_2 we give results at a few internuclear distances for the B $^3\Sigma_u^-$ and A $^3\Sigma_u^+$ states. The SCF results for the $^1\Sigma_u^+$ states of N_2 and $^3\Sigma_u^-$ states of O_2 answer some important questions concerning the relative locations of valence and Rydberg states of the same symmetry in the HF approximation compared to the positions of the corresponding states in the observed spectrum. For example, we show that in a basis with only valence atomic orbitals there is no bound $^1\Sigma_u^+$ state arising from a $\pi_u \rightarrow \pi_g$ transition in N_2 in the HF

approximation. Expansion of the basis to include Rydberg orbital character gives well defined Rydberg states but still no bound valence states. This is contrary to experiment where the π_g orbital of the $b'\ ^1\Sigma_u^+$ state is known to be strongly antibonding. We show that there is a simple explanation for this behavior, namely, that changes in correlation energy are important in establishing the ordering of these excited states. A very similar case arises in comparing the valence $B\ ^3\Sigma_u^-$ state of O_2 with configuration $(\pi_u)^3(\pi_g)^3$ and a Rydberg state of the same symmetry with the configuration $(\pi_u)^3(1\pi_g)^2(2\pi_g)$.

B. The SCF Hamiltonians

For open-shell systems the SCF wavefunction is, in general, a sum of Slater determinants. For many open-shell states it is possible to write the expression for the total energy in terms of the familiar one-electron, Coulomb and exchange integrals of closed shell SCF theory. In such cases, if one partitions the occupied spatial orbitals into Q shells each containing the set of orbitals $\{\phi_q\}$, the energy is given by

$$E = 2 \sum_{q=1}^{Q} f_q \sum_{\phi_i \in \{\phi_q\}} h_i + \sum_{q=1}^{Q} \sum_{p=1}^{Q} f_q f_p \sum_{\phi_i \in \{\phi_q\}} \sum_{\phi_j \in \{\phi_p\}} (2 a_{qp} J_{ij} - b_{qp} K_{ij}) \quad . \tag{5}$$

Here f_q is the fractional occupation of shell q, a_{qp} and b_{qp} are elements of a symmetric matrix specifying the interactions between shells q and p, and h_i, J_{ij} and K_{ij} are defined as follows,

$$h_i = \langle \phi_i | h | \phi_i \rangle \tag{6a}$$

$$J_{ij} = \langle \phi_i(1)\phi_j(2) | \frac{1}{r_{12}} | \phi_i(1)\phi_j(2) \rangle \tag{6b}$$

$$K_{ij} = \langle \phi_i(1)\phi_j(2) | \frac{1}{r_{12}} | \phi_j(1)\phi_i(2) \rangle . \tag{6c}$$

The numbers a_{qp} and b_{qp} must be determined for each specific state. Requiring that the energy be stationary with respect to variations of the orbitals, we obtain the HF equation for each shell,

$$F_q \phi_i = \epsilon_i \phi_i \tag{7a}$$

$$F_q = h + \sum_{p=1}^{Q} f_p \sum_{\phi_j \epsilon \{\phi_p\}} (2 a_{qp} J_j - b_{qp} K_j) . \tag{7b}$$

The off-diagonal Lagrange multipliers, ϵ_{ij}, needed to preserve orthogonality between orbitals ϕ_i and ϕ_j are not explicitly shown in Eq. (7a) since we assume that these equations are to be solved by the OCBSE method.[2] In this method the orthogonality of a given orbital to all others is achieved by requiring the variations to be orthogonal to the other orbitals.

Clearly if the energy, Eq. (5), cannot be written only in terms of the integrals h_i, J_{ij} and K_{ij}, then the resulting SCF equations, Eqs. (7), will contain operators which cannot be expressed in terms of the Coulomb and exchange operators. The resulting equations would be more complicated to solve numerically, requiring an SCF program which would have to manipulate the additional integrals necessary for the calculation. Huzinaga has stated that the energy expressions for some important excited Σ states of diatomic molecules cannot be written in terms of J and K integrals alone.[1] These would include the $b' \, {}^1\Sigma_u^+$ state of N_2 and the $B \, {}^3\Sigma_u^-$ of O_2. However, if the wavefunctions of the configuration $(1\pi)^n(2\pi)^m$ are expressed in terms of the real functions π_x and π_y instead of the complex functions π^+ and π^-, the terms in the energy expression which are not obviously J and K integrals are of only three types:

$$I_1 = \langle 1\pi_x(1)2\pi_x(2) | \frac{1}{r_{12}} | 1\pi_y(1)2\pi_y(2) \rangle \tag{8a}$$

$$I_2 = \langle 1\pi_x(1)1\pi_y(2) | \frac{1}{r_{12}} | 2\pi_x(1)2\pi_y(2) \rangle \tag{8b}$$

$$I_3 = \langle 1\pi_x(1)1\pi_y(2) | \frac{1}{r_{12}} | 2\pi_y(1)2\pi_x(2) \rangle . \tag{8c}$$

Through various algebraic identities, I_1, I_2, and I_3 can all be expressed in terms of Coulomb and exchange integrals. The expression for I_1 can be obtained from the relationship

$$\langle 1\pi^-(1)2\pi^-(2) | \frac{1}{r_{12}} | 1\pi^+(1)2\pi^+(2) \rangle = 0 = 2\, J(1\pi_x, 2\pi_x) - 2\, J(1\pi_x, 2\pi_y) - 4\, I_1 . \tag{9}$$

Hence,

$$I_1 = \frac{J(1\pi_x, 2\pi_x) - J(1\pi_x, 2\pi_y)}{2} . \tag{10}$$

Here π^+ and π^- are $(\pi_x + i\pi_y)/\sqrt{2}$ and $(\pi_x - i\pi_y)/\sqrt{2}$, respectively. Similarly I_2 can be found from

$$\langle 1\pi^-(1)1\pi^-(2) | \frac{1}{r_{12}} | 2\pi^+(1)2\pi^+(2) \rangle = 0 = 2\, K(1\pi_x, 2\pi_x) - 4\, K(1\pi_x, 2\pi_y) - 2\, I_2 . \tag{11}$$

Hence,

$$I_2 = K(1\pi_x, 2\pi_x) - 2\, K(1\pi_x, 2\pi_y) . \tag{12}$$

Finally I_3 is just an exchange integral

$$I_3 = K(1\pi_x, 2\pi_y) . \tag{13}$$

These results for I_1, I_2 and I_3 can now be used to write the energy expressions for the open-shell Σ states of the configuration $(1\pi)^n(2\pi)^m$ in terms of J and K integrals only. With the resulting coefficients a_{qp} and b_{qp}, calculations can be done for these states using existing open-shell SCF programs. Tables I and II give these coefficients for the various states of the configuration $\pi_u^3 \pi_g$ and $\pi_u^3 \pi_g^3$, respectively. These states include many of the valence excited states of N_2 and O_2. All the results for the $\pi_u^3 \pi_g$ configuration are applicable to CO also, although the π orbitals no longer have g or u symmetry. The results for the Δ states are not new but are included for completeness.

TABLE I. Coefficients for the configuration $\pi_u^3 \pi_g$.[a]

State	q =	σ	π_{ux}	π_{uy}	π_{gx}	π_{gy}
all states	f_q	1	3/4	3/4	1/4	1/4
	$(a_{\sigma q}, b_{\sigma q})$	(1, 1)	(1, 1)	(1, 1)	(1, 1)	(1, 1)
	$(a_{\pi_{ux} q}, b_{\pi_{ux} q})$	(1, 1)	(8/9, 8/9)	(8/9, 8/9)	b	b
$^3\Sigma_u^+$	$(a_{\pi_{gx} q}, b_{\pi_{gx} q})$	(1, 1)	(1/3, 4/3)	(5/3, 4/3)		
$^1\Sigma_u^+$	$(a_{\pi_{gx} q}, b_{\pi_{gx} q})$	(1, 1)	(1/3, -4)	(5/3, 20/3)		
$^3\Sigma_u^-$, $^1\Sigma_u^-$	$(a_{\pi_{gx} q}, b_{\pi_{gx} q})$	(1, 1)	(5/3, 4/3)	(1/3, 4/3)		
$^3\Delta_u$	$(a_{\pi_{gx} q}, b_{\pi_{gx} q})$	(1, 1)	(1, 4/3)	(1, 4/3)		
$^1\Delta_u$	$(a_{\pi_{gx} q}, b_{\pi_{gx} q})$	(1, 1)	(1, 4/3)	(1, -4)		

[a]The coefficients not explicitly listed can be found by a transformation $x \rightarrow y$ in the row and column labels. A blank space indicates no interaction.

[b]These coefficients vary from state to state and can be found lower in the table by utilizing the symmetry of a_{pq} and b_{pq}.

TABLE II. Coefficients for the configuration $\pi_u^3 \pi_g^3$.[a]

State	q =	σ	π_{ux}	π_{uy}	π_{gx}	π_{gy}
all states	f_q	1	3/4	3/4	3/4	3/4
	$(a_{\sigma q}, b_{\sigma q})$	(1, 1)	(1, 1)	(1, 1)	(1, 1)	(1, 1)
	$(a_{\pi_{ux} q}, b_{\pi_{ux} q})$	(1, 1)	(8/9, 8/9)	(8/9, 8/9)	b	b
$^3\Sigma_u^+$	$(a_{\pi_{gx} q}, b_{\pi_{gx} q})$	(1, 1)	(11/9, 4/3)	(7/9, 4/3)	(8/9, 8/9)	(8/9, 8/9)
$^1\Sigma_u^+$	$(a_{\pi_{gx} q}, b_{\pi_{gx} q})$	(1, 1)	(11/9, 4/9)	(7/9, 4/9)	(8/9, 8/9)	(8/9, 8/9)
$^3\Sigma_u^-$	$(a_{\pi_{gx} q}, b_{\pi_{gx} q})$	(1, 1)	(7/9, 4/9)	(11/9, 20/9)	(8/9, 8/9)	(8/9, 8/9)
$^1\Sigma_u^-$	$(a_{\pi_{gx} q}, b_{\pi_{gx} q})$	(1, 1)	(7/9, 4/3)	(11/9, -4/9)	(8/9, 8/9)	(8/9, 8/9)
$^3\Delta_u$	$(a_{\pi_{gx} q}, b_{\pi_{gx} q})$	(1, 1)	(1, 4/3)	(1, 4/9)	(8/9, 8/9)	(8/9, 8/9)
$^1\Delta_u$	$(a_{\pi_{gx} q}, b_{\pi_{gx} q})$	(1, 1)	(1, 4/9)	(1, 4/3)	(8/9, 8/9)	(8/9, 8/9)

TABLE II. Continued.

[a]The coefficients not explicitly listed can be found by the transformation $x \rightarrow y$ in the row and column labels.

[b]These coefficients vary from state to state and can be found lower in the table by utilizing the symmetry of a_{pq} and b_{pq}.

C. Excited States of N_2 and CO

Tables III and IV give the results of SCF calculations on many of the interesting excited states of N_2 and CO. In addition to the states arising from the $\pi \rightarrow \pi^*$ excitation, we also give results for the $\sigma \rightarrow \pi^*$ valence states and some ions. SCF results have already been reported for the a $^3\Pi$ state of CO[3] and the X $^2\Sigma_g^+$ and A $^2\Pi_u$[4] ions of N_2, but the results for the other excited states are presented for the first time mainly due to the historical difficulties of expressing the open-shell SCF Hamiltonians of the $^{1,3}\Sigma^+$, and $^{1,3}\Sigma^-$ states in terms of Coulomb and exchange operators only.[1] The results of the previous section now allow us to carry out SCF calculations on these states in a simple and direct way. All the calculations except those for the $^1\Sigma_u^+$ state of N_2 were done in a valence [4s3p] contracted Gaussian basis derived from a (9s5p) primitive basis on each atom.[5] This basis gives an SCF energy close to the HF limit for the ground states, i.e., -108.9928 a.u. for N_2[4] and -112.7860 a.u. for CO.[6] The effect of adding Rydberg-like $p\pi$ orbitals to the basis is estimated to be less than 0.001 a.u. on the total energy of the valence states listed. Although addition of a single $d\pi$ function to the basis in N_2 lowers the ground state energy by 0.071 a.u., the changes in excitation energies are much smaller, e.g., an increase of 0.27 eV for the X $^1\Sigma_g^+ \rightarrow$ A $^3\Sigma_u^+$ transition.

The results are in good agreement with experiment except for the b' $^1\Sigma_u^+$ state of N_2 and the $^1\Sigma^+$ ($1\pi \rightarrow 2\pi$) of CO where there

TABLE III. SCF results for the excited states of N_2.[a]

State	Description[b]	E_{SCF} (au)	ΔE_{exp}[c] (eV)	ΔE_{SCF} (eV)	ΔE_{fc} (eV)
$X\ ^1\Sigma_g^+$		-108.8877	0.0	0.0	0.0
$B\ ^3\Pi_g$	$\sigma_g \rightarrow \pi_g$	-108.6064	8.1	7.66	7.78
$a\ ^1\Pi_g$	$\sigma_g \rightarrow \pi_g$	-108.5408	9.3	9.44	9.72
$A\ ^3\Sigma_u^+$	$\pi_u \rightarrow \pi_g$	-108.6613	7.8	6.16	6.22
$^1\Sigma_u^+$	Rydberg[d]	-108.3633		14.27[d]	—
$a'\ ^1\Sigma_u^-$	$\pi_u \rightarrow \pi_g$	-108.5813[e]	9.9	8.34	8.38
$^3\Delta_u$	$\pi_u \rightarrow \pi_g$	-108.6211	8.5	7.26	7.31
$^1\Delta_u$	$\pi_u \rightarrow \pi_g$	-108.5565	10.3	9.01	9.05
$X\ ^2\Sigma_g^+$	N_2^+	-108.3059	15.6	15.83	17.05
$A\ ^2\Pi_u$	N_2^+	-108.3063	17.1	15.82	16.97

TABLE III. Continued.

[a]At an internuclear distance of 1.094 Å.

[b]This describes the excitation relative to the ground state configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$.

[c]These values taken from R. S. Mulliken, "The Energy Levels of the Nitrogen Molecule" in the Threshold of Space, edited by B. Armstrong and A. Dalgarno (Pergamon Press, Inc., New York, 1957) and F. R. Gilmore, J. Quant. Spectrosc. Radiat. Transfer 5, 369 (1965).

[d]This is not the b′ $^1\Sigma_u^+$ state which is known to have a strongly antibonding π_g orbital but is a Rydberg state with the configuration (core)$(\pi_u)^3(3\sigma_g)^2 nd\pi_g$. No bound state of this symmetry is obtained with a purely valence basis. See text for discussion.

[e]In the HF approximation the B′ $^3\Sigma_u^-$ and a′ $^1\Sigma_u^-$ states have the same energy. Experimentally the B′ $^3\Sigma_u^-$ state lies at about 9.0 eV.

TABLE IV. SCF results for the excited states of CO.[a]

State	Description[b]	E_{SCF} (au)	ΔE_{exp}[c] (eV)	ΔE_{SCF} (eV)	ΔE_{fc} (eV)	D_{exp}[d]	D_{SCF}[d]
$X\ ^1\Sigma^+$		-112.6969	0.0	0.0	0.0	-0.114 ± 0.005	0.528
$a\ ^3\Pi$	$\sigma \rightarrow \pi^*$	-112.4977	6.3	5.42	5.80	± 1.38	2.33
$A\ ^1\Pi^e$	$\sigma \rightarrow \pi^*$	-112.3837	8.35	8.52	9.10	±0.03 ± 0.08	1.29
$a\ ^3\Sigma^+$	$\pi \rightarrow \pi^*$	-112.4492	8.2	6.74	7.65		-1.45
$I\ ^1\Sigma^-$	$\pi \rightarrow \pi^*$	-112.3981[f]	9.1	8.13	9.44		-1.11
$d\ ^3\Delta$	$\pi \rightarrow \pi^*$	-112.4225	9.1	7.46	8.55		-1.28
$D\ ^1\Delta$	$\pi \rightarrow \pi^*$	-112.3890	10.4	8.38	9.95		-0.95
$X\ ^2\Sigma^+$	CO^+	-112.1990	14.1	13.55	15.18		

[a]At an internuclear distance of 1.128 Å.

[b]This describes the excitation relative to the ground state configuration $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$.

[c]See P. H. Krupenie, "The Band Spectrum of CO," National Standard Reference Data Series, NBS 5 (1966).

TABLE IV. Continued.

[d]In Debyes. The dipole moment is positive if charge is transferred from carbon to oxygen, i.e., carbon is positive. The experimental values for the a $^3\Pi$ and A $^1\Pi$ states are for the equilibrium distances on these states, i.e., 1.21 Å and 1.235 Å, respectively.

[e]The total HF oscillator strength for this transition is 0.185 which is very close to experiment. See Ref. 11.

[f]In the HF approximation the e $^3\Sigma^-$ and I $^1\Sigma^-$ states have the same energy. Experimentally the e $^3\Sigma^-$ state lies at about 8.9 eV.

are some serious problems in attempting SCF calculations. We discuss these below. In most cases the SCF scheme underestimates the excitation energies since the excited states would usually have less correlation energy than the ground state. This is not so for some cases, for example, the $b'\,^1\Sigma_u^+$ state of N_2 and the $B\,^3\Sigma_u^-$ of O_2. The results in column 6 of Tables III and IV are those in which only the excited orbital, e.g., π_g, is variationally determined and the core orbitals are taken from the ground state calculation. This approximation is quite good for N_2 but unsufficient for CO, e.g., in the $^1\Delta$ state of CO core contraction lowers the energy by 1.6 eV. Nesbet[7] has computed the energy levels of all these states in the simple virtual orbital approximation. They are, in general, about 1 eV higher than our frozen-core results for N_2 but the discrepancy is less for CO.

The $^1\Sigma^+$ states of N_2 and CO are of special interest since they illustrate a serious problem with the SCF approach to some excited states. In N_2 the $b'\,^1\Sigma_u^+$ state is primarily a $\pi_u \rightarrow \pi_g$ transition with a vertical excitation energy of about 14.4 eV. Experimentally there is a strong perturbation of the $b'\,^1\Sigma_u^+$ state by the $c'\,^1\Sigma_u^+$ state, but this estimate of 14.4 eV for excitation to the $b'\,^1\Sigma_u^+$ is the deperturbed value of Geiger and Schröder.[8] A vibrational analysis shows the $b'\,^1\Sigma_u^+$ state to have a strongly anti-bonding π_g orbital and an equilibrium internuclear distance of 1.44 Å. In the SCF scheme no bound valence state exists which has such characteristics. In a [4s3p] Gaussian basis with only valence atomic orbitals,[5] only π_g orbitals with positive eigenvalues result from the SCF iterative scheme. When very diffuse Rydberg-like atomic orbitals are added to the basis, i.e., p_x and p_z orbitals with exponents of 0.05, 0.015, 0.004, and 0.001, rapid convergence to a $^1\Sigma_u^+$ with a Rydberg-like π_g orbital results. This is a Rydberg state with an

oscillator strength[9] of 0.033 and a mean-squared displacement for the π_g orbital of $\langle \pi_g | x^2 | \pi_g \rangle = 50.2$ a.u.^{2} (this is a ndπ orbital lying in the x-z plane where z is the molecular axis). The state is well described in the frozen core approximation using an ionic A $^2\Pi_u$ core, e.g., the energy lowering due to self-consistency is less than 0.01 eV. This state is then the first in a $^1\Sigma_u^+$ Rydberg series with the configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(\pi_u)^3(3\sigma_g)^2 nd\pi_g$ and a HF excitation energy of 14.27 eV or 1.55 eV below the A $^2\Pi_u$ ion in the HF scheme. With this term value this state should be experimentally at about 15.6 eV, i.e., 1.55 eV below the true ionization potential. There are many Rydberg transitions appearing in this region in the energy-loss spectrum of Geiger and Stickel.[10]

The question now arises as to where the valence-like b' $^1\Sigma_u^+$ state of N_2 is. The explanation is that in HF theory this valence state is calculated to be above the HF ionization potential and therefore in the continuum of the A $^2\Pi_u$ ion. Because of orthogonality requirements the state is also contaminated with lower-energy Rydberg components. This argument suggests a HF excitation energy of at least 15.8 eV and implies that the valence excited b' $^1\Sigma_u^+$ state has about 1.5 eV more correlation energy than the ground state. This is not unique as we will show that the B $^3\Sigma_u^-$ state of O_2 has 2.5-3 eV more correlation energy than the ground X $^3\Sigma_g^-$ state.

We also find no bound valence-like $\pi \rightarrow \pi^*$ state of $^1\Sigma^+$ symmetry for CO in the HF approximation and in fact such a state has not been observed. Lefebvre-Brion et al.,[11] have shown that the

B $^1\Sigma^+$ and C $^1\Sigma^+$ states (at 10.78 eV and 11.40 eV experimentally)[12] must be $\sigma \rightarrow \sigma^*$ excitation in which the σ^* orbital contains primarily M shell atomic functions. Calculations using the X $^2\Sigma^+$ ion core of CO and including Rydberg basis functions give $^1\Sigma^+$ states at 3.3 eV and 2.5 eV below the X $^2\Sigma^+$ ion. Using an ionization potential of 14.1 eV for this ion these states come out at 10.8 eV and 11.6 eV, respectively, in good agreement with experiment.[12] The calculated oscillator strengths of 0.031 and 0.082 for the transitions to the B and C states are in good qualitative agreement with the experimental values of 0.017 and 0.170.[12]

Dipole moments are also shown for CO in Table IV. The ground state dipole moment is opposite to the observed value and quite far from the HF limit of about 0.274 D.[6] Hence, the calculated values should probably be viewed as representing only differences in dipole moments reliably. The Σ and Δ states are predicted to have large dipole moments in the same direction as the ground state (C^-O^+), which may be verified experimentally, while the Π states have large positive moments (C^+O^-). The dipole moment of the a $^3\Pi$ state (essentially the same value, 2.46 D, was obtained by Huo[12]) is very large and in qualitative agreement with experiment (1.38 D).

D. Excited States of O_2

Two important excited states of O_2 are the A $^3\Sigma_u^+$ and B $^3\Sigma_u^-$ states which are the upper states in the Herzberg bands ($A \rightleftharpoons X$) and Schumann-Runge bands ($B \rightleftharpoons X$) respectively. The transition $X \rightarrow B$ is dipole-allowed with an oscillator strength of 0.193. These states arise from a $\pi_u \rightarrow \pi_g$ transition which leads to the relatively large increase of about 0.3 to 0.4 Å in equilibrium internuclear separation relative to the ground state. Robin and Kuebler[13] have shown that the Schumann-Runge bands are unaffected by high pressures of inert perturbing gases indicating that the B state is a valence state. However, Taketa et al.,[14] have carried out π-electron calculations which show that the A state is adequately described in a minimum basis of valence atomic orbitals but that the B state comes out too high in energy. By allowing the orbital exponent of one π_g molecular orbital (MO) to take a different value from the other π_g MO's, variational calculations showed that the resulting outermost π_g orbital is much more diffuse than the other. We will show below that these calculations did not converge to the spectroscopic B $^3\Sigma_u^-$ state but to a Rydberg $^3\Sigma_u^-$ state with an electron configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(\pi_u)^3(\pi_g)^2 nd\pi_g$. In the π-electron approximation without exchange with the core, this Rydberg $^3\Sigma_u^-$ state has a lower energy than the valence state $[(\text{core})(\pi_u)^3(\pi_g)^3]$ in the SCF approximation. In fact, Fig. 1 shows that with reasonably accurate SCF results the $(\pi_u)^3(\pi_g)^3$ state is only 0.33 eV below the $(\pi_u)^3(\pi_g)^2 nd\pi_g$ state. It is the inclusion of

electron correlation which puts the valence state 6-7 eV below the Rydberg state. Recent extensive configuration interaction calculations[15,16] confirm these conclusions.

Table V shows the results of SCF calculations on the X $^3\Sigma_g^-$, A $^3\Sigma_u^+$ and B $^3\Sigma_u^-$ states of O_2 and the a $^4\Pi_u$ state of O_2^+ at several internuclear distances. These are done using the coefficients of Table II. The vertical excitation energy for the A state is reasonable but the $^3\Sigma_u^+ - {}^3\Sigma_u^-$ separation is far too large, namely 8 eV instead of the observed 2 eV. Inclusion of a single d function on each atom only lowers the excitation energy of the B state by 0.2 eV. This separation of 8 eV would be reduced considerably by including electron correlation. Comparison of minimum basis set SCF calculations with the complete minimal basis configuration interaction results of Schaefer and Harris[17] shows that the B $^3\Sigma_u^-$ state has about 3 eV more correlation energy than the X $^3\Sigma_g^-$ state. From Table V we see that on the other hand the A $^3\Sigma_u^+$ state has 2 eV less correlation energy than the ground state. These two effects then reduce the SCF $^3\Sigma_u^+ - {}^3\Sigma_u^-$ separation of 8 eV to about 3 eV.

To clarify the question of the relative location of the valence $^3\Sigma_u^-$ state and a Rydberg state of the same symmetry in the SCF approximation as compared to experiment, we have solved directly for the $^3\Sigma_u^-$ state with the configuration $(\text{core})(\pi_u)^3(\pi_g)^2 2\pi_g$. This state then has a singly-occupied diffuse $2\pi_g$ orbital and a doubly-occupied valence π_g orbital. There are four possible spin couplings for such a state[14] but since only Rydberg states are of interest we

TABLE V. Some valence states of O_2.[a]

State	Description	E_{SCF} (R)					Vertical excitation energy		R_e	
		1.0	1.207	1.42	1.60	1.80	Exp	SCF	Exp	SCF
$X\ ^3\Sigma_g^-$	ground	-149.4670	-149.5758	-149.5211	-149.4411				1.21	1.21 ∓ 0.02
$A\ ^3\Sigma_u^+$	$\pi_u \rightarrow \pi_g$		-149.4276	-149.5057	-149.5027	-149.4745	6.2	4.03	1.52	1.49 ∓ 0.04
$B\ ^3\Sigma_u^-$[b]	$\pi_u \rightarrow \pi_g$		-149.1110	-149.1558	-149.1254	-149.0701	8.3	12.64	1.60	1.4-1.5[c]
$a\ ^4\Pi_u$	O_2^+	-148.8244	-149.0437	-149.0617	-149.0246		16.7	14.48	1.38	1.34 ∓ 0.02

[a] In a [4s3p] Gaussian basis. See Ref. 5.

[b] The SCF value of the oscillator strength for the X → B transition is 0.87.

[c] Due to incorrect dissociation the potential energy curve begins rising steeply near equilibrium causing R_e to be underestimated.

can choose a state such that the core corresponds to the lowest state of O_2^+ with the configuration (core)$(\pi_u)^3(\pi_g)^2$. This is the a $^4\Pi_u$ state. The wavefunction for this Rydberg $^3\Sigma_u^-$ state is then

$$\Psi(^3\Sigma_u^-) = \mathcal{A}\{3(\pi_{ux}\pi_{ux}\pi_{uy}2\pi_{gy} + \pi_{uy}\pi_{uy}\pi_{ux}2\pi_{gx})\alpha\beta\alpha\beta\,\pi_{gx}\pi_{gy}\alpha\alpha$$

$$- (\pi_{ux}\pi_{ux}\pi_{uy}2\pi_{gy} + \pi_{uy}\pi_{uy}\pi_{ux}2\pi_{gx})\alpha\beta\beta\alpha\pi_{gx}\pi_{gy}\alpha\alpha \qquad (14)$$

$$- (\pi_{ux}\pi_{ux}\pi_{uy}2\pi_{gy} + \pi_{uy}\pi_{uy}\pi_{ux}2\pi_{gx})\alpha\beta\alpha\alpha\,\pi_{gx}\pi_{gy}(\alpha\beta + \beta\alpha)\}.$$

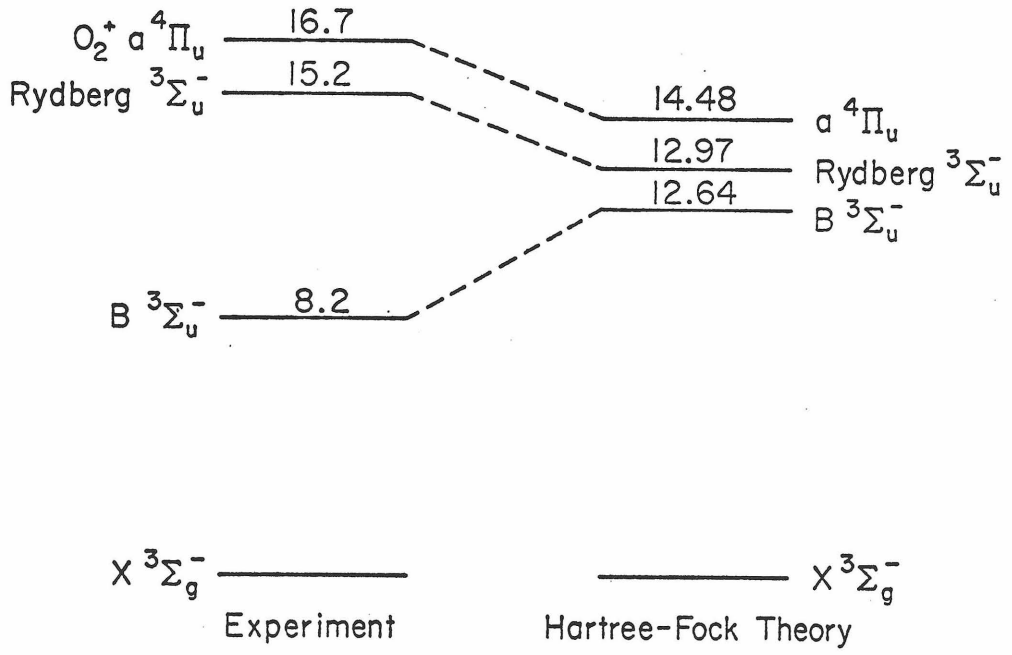
In Eq. (14) $\mathcal{A}$ is the antisymmetrizer and we do not show the sigma orbitals for convenience. The function, Eq. (14), reduces to that for the $(\pi_u)^3(\pi_g)^3$ configuration if the Rydberg orbital $2\pi_g$ is set equal to π_g. Table VI shows the a_{pq} and b_{pq} coefficients needed in the SCF calculations. The valence electron interactions are identical to those of the a $^4\Pi_u$ ion. The SCF energy for this Rydberg state is -149.0990 a.u. Its Rydberg character is reflected by its low oscillator strength of 0.001 and a very diffuse $2\pi_g$ orbital, e.g., with a matrix element $\langle 2\pi_g|x^2|2\pi_g\rangle$ = 60.1 a.u.^{2} compared to $\langle 1\pi_g|x^2|1\pi_g\rangle$ = 1.11 a.u.^{2} The Rydberg $^3\Sigma_u^-$ state is only 0.33 eV above the valence B $^3\Sigma_u^-$ state in the SCF approximation, whereas experimentally the $^3\Sigma_u^-$ state is about 7 eV above the B $^3\Sigma_u^-$. Electron correlation is responsible for a large part of this difference. Figure I illustrates these differences clearly.[18] It is clear that in the π-electron approximation, without exchange, the Rydberg

TABLE VI. Coefficients for the $[(\pi_u)^3(\pi_g)^2 2\pi_g]\ ^3\Sigma_u^-$ Rydberg state.[a]

q =	σ	π_{ux}	π_{uy}	π_{gx}	π_{gy}	$2\pi_{gx}$	$2\pi_{gy}$
f_q	1	3/4	3/4	1/2	1/2	1/4	1/4
$(a_{\pi_{ux}q}, b_{\pi_{ux}q})$	(1, 1)	(8/9, 8/9)	(8/9, 8/9)	(1, 4/3)	(1, 4/3)	(1/3, -20/9)	(5/3, 44/9)
$(a_{\pi_{gx}q}, b_{\pi_{gx}q})$	(1, 1)	(1, 4/3)	(1, 4/3)	(1, 2)	(1, 2)	(1, -2/3)	(1, -2/3)
$(a_{2\pi_{gx}q}, b_{2\pi_{gx}q})$	(1, 1)	(1/3, -20/9)	(5/3, 44/9)	(1, -2/3)	(1, -2/3)	(1, -2/3)	

[a]The other coefficients for the π_{uy}, π_{gy}, and $2\pi_{gy}$ orbitals can be obtained from the transformation x → y in the row and column labels. σ refers to the closed shell core.

FIG. I. Correlation between Hartree-Fock theory and experiment for the valence B $^3\Sigma_u^-[(\pi_u)^3(\pi_g)^3]$ and the Rydberg $^3\Sigma_u^-[(\pi_u)^3(\pi_g)^2 2\pi_g]$ states. See text for discussion.



$^3\Sigma_u^-$ state lies below the B $^3\Sigma_u^-$ state, explaining why the calculation of Taketa et al.,[14] converged to the Rydberg state. The valence $(\pi_u)^3(\pi_g)^3$ state, which is constrained to have equivalent π_g orbitals certainly represents the major configuration of the Schumann-Runge state. For example, it indicates an equilibrium internuclear separation of about 1.4-1.5 Å[19] compared to the experimental value of 1.6 Å. On the other hand the Rydberg $^3\Sigma_u^-$ state[20] has a SCF equilibrium separation of 1.34 Å, in good agreement with the experimental value which should be close to 1.38 Å of the a $^4\Pi_u$ state of O_2^+.[21] Other molecular properties which are sensitive to correlation, e.g., the oscillator strength can be expected to be in error since the $\pi_u \rightarrow \pi_g$ transition represents only about 80% of the Schumann-Runge state,[15,16] most of the remainder being a $3\sigma_g \rightarrow 3\sigma_u$ contribution.[22]

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19. This can only be an estimate since the HF wavefunction dissociates incorrectly and this forces the potential energy curve to begin rising sharply.

20. A Rydberg state with the configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2\,2\sigma_u(3\sigma_g)^2$ $(\pi_u)^4(\pi_g)^2 nd\pi_g$ has been observed with a term value of 1.49 eV. This is relative to $^4\Sigma_u^-$ core of O_2^+. This supports our estimate of 1.51 eV for the term value of the $^3\Sigma_u^-$ Rydberg state.

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III. APPENDIX

Equations-of-Motion Method Including Renormalization and Double-Excitation Mixing*

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Abstract:

The equations-of-motion method is discussed as an approach to calculating excitation energies and transition moments directly. The proposed solution [T. Shibuya and V. McKoy, Phys. Rev. A, 2, 2208 (1970)] of these equations is extended in two ways. First we include the proper renormalization of the equations with respect to the ground state particle-hole densities. We then show how to include the effects of two-particle-hole components in excited states which are primarily single-particle-hole states. This is seen to be equivalent to a single-particle-hole theory with a normalized interaction. Applications to various diatomic and polyatomic molecules indicate that the theory can predict excitation energies and transition moments accurately and economically.

I. INTRODUCTION

The conventional approach to predicting the excitation energy of an excited state of a molecule would be to solve Schroedinger's equation separately for the energies and wavefunctions of the ground and excited state. In this way one calculates the total energies and absolute wavefunctions of two states in order to calculate the excitation energy. In spectroscopy the quantities of direct physical interest in a transition are excitation frequency and oscillator strength and not really the total energies and wavefunctions of the states. On the other hand the equations-of-motion method[1] attempts to calculate the excitation frequency of a transition directly. Observables such as the excitation energy of an excited state and its transition matrix elements involve not so much the total wavefunctions as certain relationships between them. Accordingly in the equations-of-motion method one calculates excitation operators rather than wavefunctions.

An excitation operator, O_λ^+, relates one state $|\lambda>$ to the ground state $|0>$ through a set of amplitudes. These amplitudes and an excitation frequency are the solution of the equations of motion. In summary, the philosophy of this approach is to shift emphasis away from absolute quantities such as total energies and to concentrate on the relative quantities e. g. excitation energies, directly accessible to measurement.[1]

The main objective of the equations-of-motion method is to obtain excitation energies of excited states relative to a correlated ground state directly. Thus the excitations are out of a correlated

ground state. This provides some definite advantages over an approximation in which the excited state wavefunction is correlated but the Hartree-Fock (HF) wavefunction is used for the ground state. With a correlated ground state potential energy curves should dissociate to the correct dissociation limits. Moreover the results in this approximation satisfy the energy-weighted sum rule which for electric dipole transitions is the Thomas-Reiche-Kuhn theorem.[2] This is very useful if one is looking at various electric dipole transitions of a molecule since the predicted intensities would be distributed in a way consistent with the sum rule. Finally, Harris[3] has shown that in the time-dependent HF approximation, which is just the lowest order solution to the equations of motion with an implied correlated ground state, the different expressions for the oscillator strengths are equivalent with one another. If the dipole velocity and length forms of the oscillator strength disagree with each other in a basis set calculation, the difficulty is in the finite basis set. This result can be very useful in practical applications. Harris[3] also shows that in this approximation the two expressions for the rotational strength are also equivalent. There is no origin dependence and the rotational strength sum rule holds. These properties are necessary for a theory to have wide applicability in spectroscopy.

Recently we proposed a solution of the equations of motion which should be practical and accurate enough for describing the electronically excited states of molecules.[4] We started from Rowe's variational form of the equations of motion[1] which states that the

operator O_λ^+ for creating an excited state $|\lambda>$ from the ground state is exactly a solution of the equation

$$<0|[\delta O_\lambda,\ H,\ O_\lambda^+]|0> = \omega_\lambda <0|[\delta O_\lambda,\ O_\lambda^+]|0> \qquad (1)$$

where ω_λ is the excitation energy $(E_\lambda - E_0)$ and the double commutator is defined by

$$2[A,\ H,\ B] = [A,\ [H,\ B]] + [[A,\ H],\ B] \qquad (2)$$

The operator O_λ^+ contains a set of amplitudes determining the relative importance of various particle-hole excitations in generating the state $|\lambda>$ out of $|0>$ i.e.,

$$O_\lambda^+ \ |0> \ = \ |\lambda> \qquad (3)$$

We obtain these amplitudes and the excitation frequency ω_λ from the solution of Eq. (1). One must assume some approximate ground state $|\phi>$ to evaluate the expectation values of the commutators in Eq. (1). However, the commutators will be of lower particle-rank than the operators themselves and hence their expectation values should depend on relatively simple properties of the ground state.

For example, the operator $a_i^+ a_m H\ a_n^+ a_j$ is of a particle-rank two greater than the operator $[a_i^+ a_m,\ H,\ a_n^+ a_j]$. This is a particular merit of the equations-of-motion method. If one evaluates Eq. (1) using the HF wavefunction as the approximate ground state and O_λ^+ with single-particle-hole creation and destruction operators the resulting equations are those of the random phase approximation

(RPA). For some cases this approximation leads to instabilities in Eq. (1).[5] In reference 4 we proposed a higher order solution to Eq. (1) in which, with the same O_λ^+ as in the RPA, the expectation values of the commutators were explicitly expanded in powers of the correlation coefficients of the ground state. These equations referred to as the higher RPA [6] gave encouraging results for the N→V and N→T transitions of ethylene.[7]

In this paper we improve the theory of reference 4 in two respects. First we include the proper renormalization of the equations due to the particle-hole densities of the ground state. The resulting equations now contain renormalized matrix elements and amplitudes but the same matrix form. Secondly, we discuss ways of estimating the effect of two-particle-hole states on the excitation energy of an excited state. Generally the most important components of an excited state are the singly excited configurations, i.e. single-particle-hole pairs. In the complete expansion of the excitation operator O_λ^+ these would have the largest amplitudes. However, for some states doubly excited configurations (relative to the ground state) can affect the excitation energy by a few electron volts. We also illustrate how the theory including two-particle-hole states is equivalent to the single-particle-hole theory with a renormalized interaction.[8, 9]

II. A SUMMARY OF VARIOUS APPROXIMATIONS

In Eq. (1) one must specify which type of excitations are to be included in the excitation operator O_λ^+ and which approximate ground state wavefunction will be used to evaluate the expectation values of the commutators. For atomic and molecular systems singly excited configurations are the most important in low-lying excited states and hence O_λ^+ contains only single-particle-hole operators (1p-1h). If we completely accept the Hartree-Fock approximation for the ground state then O_λ^+ is, in second quantized form,[10]

$$O^+(\lambda SM) = \sum_{m\gamma} Y_{m\gamma}(\lambda S)\, C^+_{m\gamma}(SM) \tag{4}$$

where $Y_{m\gamma}$ is the amplitude for the $m\gamma$ particle-hole pair and $C^+_{m\gamma}(SM)$ are spin-adapted creation operators defined by

$$C^+_{m\gamma}(00) = \frac{1}{\sqrt{2}}\left[c^+_{m\alpha}c_{\gamma\alpha} + c^+_{m\beta}c_{\gamma\beta}\right] \tag{5a}$$

$$C^+_{m\gamma}(1M) = \begin{cases} -c^+_{m\alpha}c_{\gamma\beta} & M = +1 \\ \frac{1}{\sqrt{2}}\left[c^+_{m\alpha}c_{\gamma\alpha} - c^+_{m\beta}c_{\gamma\beta}\right] & M = 0 \\ c^+_{m\beta}c_{\gamma\alpha} & M = -1 \end{cases} \tag{5b}$$

m specifies a particle state and γ a hole state, while α and β are the usual spin functions. The operators $c^+_{i\alpha}$ and c_i are creation and annihilation operators for spin-orbital $i\alpha$. Note that $C^+_{m\gamma}(SM)$

creates a state with spin symmetry SM when it acts on a singlet state.

With $O^+(\lambda SM)$ of Eq. (4) and a HF state the excitation energy of state $|\lambda>$ relative to the HF energy of the ground state is given by

$$\underset{\sim}{\underset{\sim}{A}}^{0}(S)\ \underset{\sim}{Y}(\lambda S) = \omega(\lambda S)\ \underset{\sim}{Y}(\lambda S) \qquad (6)$$

where

$$A^{0}{}_{m\gamma,\,n\delta}(S) \equiv <HF|[\,C_{m\gamma}(SM),\ H,\ C^{+}_{n\delta}(SM)]\,|HF>$$

$$= \delta_{mn}\delta_{\gamma\delta}(\epsilon_m - \epsilon_\gamma) - V_{m\delta m\gamma} + \delta_{S,0}\,(2V_{m\delta\gamma n}) \qquad (7)$$

In Eq. (7) ϵ_i is the HF orbital eigenvalue and

$$V_{ijkl} \equiv \langle i(1)\ j(2)|\ \frac{1}{r_{12}}\ |k(1)\ \ell(2)\rangle \qquad (8)$$

Eq. (6) is the usual expression for the energy from single-excitation configuration interaction (CI). In the literature of many-body physics this equation is referred to as the Tamm-Dancoff approximation (TDA).[11]

In the next approximation one simply recognizes that the HF wavefunction is not the true ground state and hence the excitation operators must include 1p-1h destruction $C_{m\gamma}$, as well as creation, $C^{+}_{m\gamma}$, operators. Thus

$$O^{+}(\lambda SM) = \sum_{m\gamma} \{Y_{m\gamma}(\lambda S)C^{+}_{m\gamma}(SM) - Z_{m\gamma}(\lambda S)\ C_{m\gamma}(\overline{SM})\} \qquad (9)$$

where

$$C_{m\gamma}(\overline{SM}) = (-1)^{S+M} C_{m\gamma}(S-M) \qquad (10)$$

If one substitutes Eq. (9) into the equation of motion and uses the HF wavefunction to evaluate the expectation values in this equation the random phase approximation is obtained:[12]

$$\begin{bmatrix} A^0(S) & B^0(S) \\ -B^{0*}(S) & -A^{0*}(S) \end{bmatrix} \begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix} = \omega(\lambda S) \begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix} \qquad (11)$$

where the elements of A^0 are defined in Eq. (7)

and

$$B^0_{m\gamma, n\delta}(S) = -\langle HF | [C_{m\gamma}(SM), H, C_{n\delta}(\overline{SM})] | HF \rangle$$

$$= -(-1)^S V_{mn\delta\gamma} + \delta_{S,O}(2V_{mn\gamma\delta}) \qquad (12)$$

Since $|0\rangle$ is the lowest state of the Hamiltonian one should require

$$O_\lambda |0\rangle = 0 \qquad \text{all } \lambda \qquad (13)$$

But in deriving the equations of the RPA, Eq. (11), we use the HF wavefunction to evaluate the expectation values of Eq. (1). The HF wavefunction does not satisfy Eq. (13) with the O^+_λ of Eq. (9). It is well known that such inconsistency may be acceptable because the equations of motion are comparatively insensitive to the approximate ground state used to set them up[1]. It is for this reason that one does not have to be very concerned about the rigorous requirement that the $|0\rangle$ used to set up the equations of motion should also satisfy Eq. (13). This also applies to the higher order approximations

we will derive below. One should, of course, check the consistency of this assumption. It is obvious that this assumption is weakest[7] for atomic and molecular calculations using minimum basis sets but improves in large basis set calculations with the increasing density of particle-hole pairs. The approximation should also be good for large numbers of particles.

To remove this inconsistency of the RPA we could use a correlated ground state wavefunction to set up the equations of motion. This leads to our next approximation.[4] The expectation values of Eq. (1) will now explicitly depend on the correlation coefficients. Exactly how these coefficients are determined is not very crucial. To a good approximation we can write the ground state wavefunction for a closed shell system as

$$|0> \simeq N_0(1 + U + \cdots)|HF> \tag{14}$$

where N_0 is the normalization constant and

$$U = \sum_{\substack{mn \\ \gamma\delta}} \{K_{m\gamma,n\delta} c^+_{m\alpha} c^+_{n\beta} c_{\delta\beta} c_{\gamma\alpha} + \frac{1}{2}(K_{m\gamma,n\delta} - K_{m\delta,n\gamma})$$

$$\times \frac{1}{2}(c^+_{m\alpha} c^+_{n\alpha} c_{\delta\alpha} c_{\gamma\alpha} + c^+_{m\beta} c^+_{n\beta} c_{\delta\beta} c_{\gamma\beta})\} \tag{15}$$

To set up a self-consistent theory we can require that the $|0>$ of Eq. (14) satisfy Eq. (13) which gives

$$Z_{m\gamma}(\lambda S) \simeq \sum_{n\delta} C^*_{m\gamma,n\delta}(S) Y_{n\delta}(\lambda S) \tag{16}$$

where

$$C_{m\gamma,\,n\delta}(S) = K_{m\gamma,\,n\delta} + (-1)^S(K_{m\gamma,\,n\delta} - K_{m\delta,\;n\gamma}) \qquad (17)$$

We can solve these equations and the equations of motion iteratively. With the wavefunction of Eq. (14) and omitting all terms quadratic and higher in the correlation coefficients, Eq. (1) becomes [4]

$$\begin{bmatrix} A(S) & B(S) \\ -B^*(S) & -A^*(S) \end{bmatrix} \begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix} = \omega(\lambda S) \begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix} \qquad (18)$$

where the matrix elements of A and B are:

$$A_{m\gamma,\,n\delta}(S) = A^0_{m\gamma,\,n\delta}(S) + \delta_{\gamma\delta}T_{mn} - \delta_{mn}T_{\gamma\delta}$$

$$B_{m\gamma,\,n\delta}(S) = B^0_{m\gamma,\,n\delta}(S) + (-1)^S S_{m\gamma,\,n\delta} + X_{m\gamma,\,n\delta}(S) \qquad (19)$$

and

$$S_{m\gamma,\,n\delta} = -\sum_{p\mu}\{V_{m\mu\delta p}\,C_{p\mu,\,n\gamma}(0) + V_{n\mu\gamma p}C_{p\mu,\,m\delta}(0)\}$$

$$T_{mn} = -\frac{1}{2}\sum_{q\mu\nu}\{V_{mq\mu\nu}C^*_{n\mu,\,q\nu}(0) + V_{\mu\nu nq}C_{m\mu,\,q\nu}(0)\}$$

$$T_{\gamma\delta} = \frac{1}{2}\sum_{pq\nu}\{V_{pq\gamma\nu}C^*_{p\delta,q\nu}(0) + V_{\delta\nu pq}C_{p\gamma,q\nu}(0)\}$$

$$X_{m\gamma,n\delta}(S) = \sum_{\mu\nu} V_{\mu\nu\gamma\delta}C_{m\mu,\,n\nu}(S) + \sum_{pq} V_{mnpq}C_{p\gamma,q\delta}(S)$$

$$-\sum_{p\mu}\{V_{m\mu p\delta}C_{p\gamma,n\mu}^{(S)} + V_{n\mu p\gamma}C_{p\delta,m\mu}^{(S)}\} \qquad (20)$$

In Eq. (20) m, n, p, q, refer to particle states, and γ, δ, μ, ν to hole states. Eqs. (16) and (18) are the higher RPA.[4] For practical purposes one need not necessarily solve these equations self-consistently but could simply estimate the correlation coefficients by perturbation theory and substitute these into Eq. (20). Usually iteration does not change the excitation frequency by more than a few per cent. This is expected since the equations are designed to be as insensitive as possible to the approximations made for the ground state. For molecular calculations with small basis sets the terms linear in the correlation coefficients in Eq. (20) are quite important.[7] Extensive calculations on the excited states of N_2 and CO also illustrate this.[13]

III. RENORMALIZATION OF THE EQUATIONS

We now show that we can obtain a more consistent set of equations than Eqs. (18)-(20) by including second-order density terms in the matrix elements $A_{m\gamma,\, n\delta}(S)$. With these additional terms we can write the equations exactly as in Eq. (18) but now with renormalized interaction matrix elements and amplitudes.

The most general equation one obtains from Eq. (1) with the 1p-1h form of O^+_λ, Eq. (9) is

$$\begin{bmatrix} \mathcal{A}(S) & \mathcal{B}(S) \\ -\mathcal{B}^*(S) & -\mathcal{A}^*(S) \end{bmatrix} \begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix} = \omega(\lambda S) \begin{bmatrix} \mathcal{D} & 0 \\ 0 & \mathcal{D}^* \end{bmatrix} \begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix} \tag{21}$$

where the matrix elements of $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{D}$ are

$$\mathcal{A}_{m\gamma,n\delta}(S) \equiv \langle 0 | [C_{m\gamma}(SM),\ H,\ C^+_{n\delta}(SM)] | 0 \rangle$$

$$\mathcal{B}_{m\gamma,n\delta}(S) \equiv -\langle 0 | [C_{m\gamma}(SM),\ H,\ C_{n\delta}(\overline{SM})] | 0 \rangle \tag{21a}$$

$$\mathcal{D}_{m\gamma,\, n\delta}(S) \equiv \langle 0 | [C_{m\gamma}(SM),\ C^+_{n\delta}(SM)] | 0 \rangle$$

In deriving the equations of the higher RPA we retained all terms linear in the correlation coefficients. These include the dominant corrections but it would be more complete to include terms in matrix elements, Eq. (21a), consistent with a given order in perturbation theory, e.g. VC and $(\epsilon_i - \epsilon_j)C^2$ are of the same order where V is an interaction matrix element and C a correlation coefficient.

To second order terms we can write

$$\mathcal{A}_{m\gamma,n\delta}(S) = A^{\circ}_{m\gamma,n\delta}(S) + \delta_{\gamma\delta}[T_{mn} - \tfrac{1}{2}(\epsilon_m + \epsilon_n - 2\epsilon_\gamma)\rho^{(2)}_{mn}]$$

$$- \delta_{mn}[T_{\gamma\delta} - \tfrac{1}{2}(2\epsilon_m - \epsilon_\gamma - \epsilon_\delta)\rho^{(2)}_{\gamma\delta}]$$

$$\mathcal{B}_{m\gamma,n\delta}(S) = B_{m\gamma,n\delta}(S) \qquad (22)$$

$$\mathcal{D}_{m\gamma,n\delta}(S) = \delta_{mn}\delta_{\gamma\delta} + \delta_{mn}\rho^{(2)}_{\gamma\delta} - \delta_{\gamma\delta}\rho^{(2)}_{mn}$$

In Eqs. (22) A° is given by Eq. (7), B by Eq. (19), and T's by Eq. (20). The $\rho^{(2)}$'s are quadratic in correlation coefficients[4]

$$\rho^{(2)}_{mn} = \tfrac{1}{2} \sum_{p\mu\nu} \sum_{S=0,1} C'_{p\mu,m\nu}(S)\, C^{*}_{p\mu,n\nu}(S)$$

$$\rho^{(2)}_{\gamma\delta} = -\tfrac{1}{2} \sum_{pq\mu} \sum_{S=0,1} C'_{p\mu q\gamma}(S) C^{*}_{p\mu,q\delta}(S) \qquad (23)$$

where the C's are defined in Eq. (17) and

$$C'_{m\gamma,n\delta}(S) = K_{m\gamma,n\delta} + (-1)^{S_1}_{\tfrac{1}{2}} (K_{m\gamma,n\delta} - K_{m\delta,n\gamma}) \qquad (24)$$

To derive Eqs. (22) we use the results

$$No^2 \simeq 1 - \langle HF | U^+U | HF \rangle$$

$$\langle HF | U^+U | HF \rangle = -\sum_{\gamma} \rho^{(2)}_{\gamma\gamma} = \sum_{m} \rho^{(2)}_{mm} \qquad (25)$$

Note that the ground state correlation energy is

$$E_{corr} = 2 \sum_{\gamma} T_{\gamma\gamma} + 2\left(\sum_{\gamma} \epsilon_{\gamma}\rho^{(2)}_{\gamma\gamma} + \sum_{m} \epsilon_{m}\rho^{(2)}_{mm}\right)$$

$$= -2 \sum_{m} T_{mm} + 2\left(\sum_{\gamma} \epsilon_{\gamma}\rho^{(2)}_{\gamma\gamma} + \sum_{m} \epsilon_{m}\rho^{(2)}_{mm}\right) \qquad (26)$$

which is just $E^{(2)}$ if the correlation coefficients of Rayleigh-Schroedinger perturbation theory are used to evaluate the T's and $\rho^{(2)}$'s leading to

$$E_{corr} = \sum_{\gamma} T_{\gamma\gamma} = - \sum_{m} T_{mm} \qquad (26a)$$

The correction term of $\mathcal{A}$ in Eq. (22) is typically about half of that of A in Eq. (19). We will see, however, that the effect of this change in the elements of $\mathcal{A}$ on the excitation frequencies is partly compensated for by renormalization terms in $\mathcal{S}$. The overall effect is usually less than 5% for the cases we have studied.[13] To a good approximation we can write:

$$\mathcal{S}_{m\gamma,n\delta} = \delta_{mn}\delta_{\gamma\delta}\left(1 + \rho^{(2)}_{\gamma\gamma} - \rho^{(2)}_{mm}\right) \qquad (27)$$

With this diagonal form for $\mathcal{S}$ Eq. (21) becomes

$$\begin{bmatrix} \bar{\mathcal{A}}(S) & \bar{\mathcal{B}}(S) \\ -\bar{\mathcal{B}}^*(S) & -\bar{\mathcal{A}}^*(S) \end{bmatrix} \begin{bmatrix} Y(\lambda S) \\ Z(\bar{\lambda}S) \end{bmatrix} = \omega(\lambda S) \begin{bmatrix} \overline{Y}(\lambda S) \\ \overline{Z}(\lambda S) \end{bmatrix} \qquad (28)$$

where the elements of $\bar{\mathcal{A}}, \bar{\mathcal{B}}, \bar{Y}$, and $\bar{Z}$ have the renormalized forms

$$\bar{\mathcal{A}}_{m\gamma,n\delta}(S) = f^{-1}_{m\gamma}\, \mathcal{A}_{m\gamma,n\delta}(S)\, f^{-1}_{n\delta}$$

$$\bar{\mathcal{B}}_{m\gamma,n\delta}(S) = f^{-1}_{m\gamma}\, \mathcal{B}_{m\gamma,n\delta}(S)\, f^{-1}_{n\delta}$$

$$\bar{Y}_{m\gamma}(\lambda S) = f_{m\gamma}\, Y_{m\gamma}(\lambda S)$$

$$\bar{Z}_{m\gamma}(\lambda S) = f_{m\gamma}\, Z_{m\gamma}(\lambda S) \qquad (28a)$$

with the renormalization factor

$$f_{m\gamma} = (1 + \rho^{(2)}_{\gamma\gamma} - \rho^{(2)}_{mm})^{\frac{1}{2}} \qquad (29)$$

A major advantage of the approximate expression Eq. (28) is that the matrices $\bar{\mathcal{A}}$ and $\bar{\mathcal{B}}$ remain symmetrical and the equations have the same form as the RPA.

The orthogonality condition implies that the amplitudes satisfy

$$\tilde{Y}^*(\lambda' S)\mathcal{B}\, Y(\lambda S) - \tilde{Z}^*(\lambda' S)\mathcal{B}^*\, Z(\lambda S) = \delta_{\lambda\lambda'} \qquad (30)$$

or, in terms of $\bar{Y}$ and $\bar{Z}$,

$$\tilde{\bar{Y}}^*(\lambda' S)\ \bar{Y}(\lambda S) - \tilde{\bar{Z}}^*(\lambda' S)\ \ Z(\lambda S) = \delta_{\lambda'\lambda} \qquad (31)$$

which again has the same form as in all the other approximations.

IV. COUPLING OF DOUBLE EXCITATIONS

The low-lying excited states of molecular systems are primarily one-electron excitations relative to the ground state. These are single-particle-hole (1p-1h) states and hence the excitation operator O_λ^+, Eq. (9), contains just 1p-1h creation and destruction operators. An excited state also contains two- and more-particle-hole components corresponding to two, three, etc., electron excitations out of the ground state. The amplitudes, $Y^{(2)}_{m\gamma,n\delta}$ and $Z^{(2)}_{m\gamma,n\delta}$, of these components of O_λ^+, will be much smaller than those of the 1p-1h components but their effect on large excitation energies e.g. 8-12 eV can be significant.[13] Their effect on transition moments will be very small. In this section we show how these 2p-2h states should be rigorously included in the theory. An important conclusion is that the theory with both 1p-1h and 2p-2h states can be shown to be equivalent to the 1p-1h theory with a renormalized interaction.[14] Finally we derive a simple and practical approximation for including the effects of these double excitations.

To include the effect of double excitations we add 2p-2h creation and destruction operators

$$\sum_{m\gamma n\delta} \{Y^{(2)}_{m\gamma,n\delta}(\lambda S)\Gamma^+_{m\gamma,n\delta}(SM) - Z^{(2)}_{m\gamma,n\delta}(\lambda S)\,\Gamma_{m\gamma,n\delta}\overline{(SM)}\} \qquad (32)$$

to the O_λ^+ of Eq. (9). Here $\Gamma^+_{m\gamma,n\delta}$ is a 2p-2h creation operator and $Y^{(2)}$ and $Z^{(2)}$ are amplitudes to be determined. The explicit expressions for Γ^+ are shown in Tables Ia and Ib. Substitution of O_λ^+ containing the

Table Ia. The 2p-2h Creation Operators $\Gamma^{+}_{m\gamma,\,n\delta}$ (S = M = 0)[a]

$$\Gamma^{+}_{m\gamma,\,m\gamma} = c^{+}_{m\alpha}\, c^{+}_{m\beta}\, c_{\gamma\beta} c_{\gamma\alpha} = C^{+}_{m\gamma}(00)\; C^{+}_{m\gamma}(00)$$

$$\Gamma^{+}_{m\gamma,\,n\gamma} = \frac{1}{\sqrt{2}}\,[\,c^{+}_{m\alpha} c^{+}_{n\beta} + c^{+}_{n\alpha} c^{+}_{m\beta}]\, c_{\gamma\beta}\; c_{\gamma\alpha} = \sqrt{2}\;\; C^{+}_{m\gamma}(00) C^{+}_{n\gamma}(00)$$
$(m \neq n)$

$$\Gamma^{+}_{m\gamma,\,m\delta} = \frac{1}{\sqrt{2}}\;\; c^{+}_{m\alpha}\;\; c^{+}_{m\beta}\,[\,c_{\delta\beta} c_{\gamma\alpha} + c_{\gamma\beta}\; c_{\delta\alpha}] = \sqrt{2}\;\; C^{+}_{m\gamma}(00) C^{+}_{m\delta}(00)$$
$(\gamma \neq \delta)$

$$\Gamma^{+}_{(m\gamma,\,n\delta)_1} = \frac{1}{2}\,[\,c^{+}_{m\alpha} c^{+}_{n\beta} + c^{+}_{n\alpha} c^{+}_{m\beta}]\,[\,c_{\delta\beta}\, c_{\gamma\alpha} + \; c_{\gamma\beta}\; c_{\delta\alpha}]$$
$(m \neq n, \gamma \neq \delta)$

$$= \frac{1}{2}\,[\,C^{+}_{m\gamma}(00) C^{+}_{n\delta}(00) + C^{+}_{m\delta}(00) C^{+}_{n\delta}(00)]$$

$$\Gamma^{+}_{(m\gamma,\,n\delta)_2} = \frac{1}{\sqrt{3}}\;\{[\,c^{+}_{m\alpha} c^{+}_{n\alpha}\, c_{\delta\alpha}\, c_{\gamma\alpha} + \; c^{+}_{m\beta} c^{+}_{n\beta}\, c_{\delta\beta}\; c_{\gamma\beta}]$$
$(m \neq n; \gamma \neq \delta)$

$$+ \frac{1}{2}\,[\,c^{+}_{m\alpha} c^{+}_{n\beta} - c^{+}_{n\alpha} c^{+}_{m\beta}]\,[\,c_{\delta\beta}\, c_{\gamma\alpha} - \; c_{\gamma\beta} c_{\delta\alpha}]\}$$

$$= \frac{1}{\sqrt{3}}\,[\,C^{+}_{m\gamma}(00) C^{+}_{n\delta}(00) - C^{+}_{m\delta}(00) C^{+}_{n\gamma}(00)]$$

[a] The subscripts on the indices for Γ^{+} indicate different spin couplings of the four orbitals, m, γ, n, and δ; there are two independent singlet excited states if $m \neq n$ and $\gamma \neq \delta$. Formal development of the equations of Sec. IV up to and including (44) does not specify these subscripts explicitly, but in fact indices describing 2p-2h excitations must include them. Starting from Eq. (45),

Table Ia. (continued)

interaction terms in $A^{0(2,2)}$ are ignored. Thus the two singlet spin couplings are degenerate, and since they are also chosen here to be orthogonal [diagonalizing the full $D^{0(2,2)}$ matrix] they can be combined into a single effective state for the index $(m\gamma, n\delta)$.

Table Ib. The 2p-2h Creation Operators $\Gamma^{+}_{m\gamma,\,n\delta}(S = 1,\ M = 0)$[a]

$$\Gamma^{+}_{(m\gamma,\,n\delta)_1} = \frac{1}{\sqrt{2}}\left[c^{+}_{m\alpha}c^{+}_{n\beta} - c^{+}_{n\alpha}c^{+}_{m\beta}\right]c_{\gamma\beta}c_{\gamma\alpha}$$

$(m \neq n)$

$$= \frac{1}{\sqrt{2}}\left[C^{+}_{m\gamma}(10)C^{+}_{n\gamma}(00) - C^{+}_{n\gamma}(10)C^{+}_{m\gamma}(00)\right]$$

$$\Gamma^{+}_{(m\gamma,\,n\delta)_1} = \frac{1}{2}\left[c^{+}_{m\alpha}c^{+}_{n\beta} - c^{+}_{n\alpha}c^{+}_{m\beta}\right]\left[c_{\delta\beta}c_{\gamma\alpha} + c_{\gamma\beta}c_{\delta\alpha}\right]$$

$(m\neq n, \gamma\neq \delta)$

$$= \frac{1}{2}\left[C^{+}_{m\gamma}(10)C^{+}_{n\delta}(00) - C^{+}_{n\delta}(10)C^{+}_{m\gamma}(00)\right.$$

$$\left. + C^{+}_{m\delta}(10)C^{+}_{n\gamma}(00) - C^{+}_{n\gamma}(10)C^{+}_{m\delta}(00)\right]$$

$$\Gamma^{+}_{(m\gamma,\,m\delta)_2} = \frac{1}{\sqrt{2}}c^{+}_{m\alpha}c^{+}_{m\beta}\left[c_{\delta\beta}c_{\gamma\alpha} - c_{\gamma\beta}c_{\delta\alpha}\right]$$

$(\gamma\neq \delta)$

$$= \frac{1}{\sqrt{2}}\left[C^{+}_{m\gamma}(10)C^{+}_{m\delta}(00) - C^{+}_{m\delta}(10)C^{+}_{m\gamma}(00)\right]$$

$$\Gamma^{+}_{(m\gamma,\,n\delta)_2} = \frac{1}{2}\left[c^{+}_{m\alpha}c^{+}_{n\beta} + c^{+}_{n\alpha}c^{+}_{m\beta}\right]\left[c_{\delta\beta}c_{\gamma\alpha} - c_{\gamma\beta}c_{\delta\alpha}\right]$$

$(m\neq n, \gamma\neq\delta)$

$$= \frac{1}{2}\left[C^{+}_{m\gamma}(10)C^{+}_{n\delta}(00) - C^{+}_{n\delta}(10)C^{+}_{m\gamma}(00)\right.$$

$$\left. - C^{+}_{m\delta}(10)C^{+}_{n\gamma}(00) + C^{+}_{n\gamma}(10)C^{+}_{m\delta}(00)\right]$$

$$\Gamma^{+}_{(m\gamma,\,n\delta)_3} = \frac{1}{\sqrt{2}}\left[c^{+}_{m\alpha}c^{+}_{n\alpha}c_{\delta\alpha}c_{\gamma\alpha} - c^{+}_{m\beta}c^{+}_{n\beta}c_{\delta\beta}c_{\gamma\beta}\right]$$

$(m\neq n, \gamma\neq\delta)$

$$= \frac{1}{\sqrt{2}} \left[C^{+}_{m\gamma}(10) C^{+}_{n\delta}(00) + C^{+}_{n\delta}(10) C^{+}_{m\gamma}(00) \right]$$

---

[a] These operators diagonalize $D^{0(2,2)}$ of Eq. (45). The subscripts on the indices $(m\gamma, n\delta)$ indicate the three possible independent spin couplings for the 2p-2h state when $m \neq n$ and $\gamma \neq \delta$. See footnote a of Table Ia.

terms in Eq. (32) into the variational form of the equations of motion, Eq. (1) gives

$$\begin{bmatrix} \mathcal{A} & \mathcal{B} \\ -\mathcal{B}^* & -\mathcal{A}^* \end{bmatrix} \begin{bmatrix} Y \\ Z \end{bmatrix} + \begin{bmatrix} \mathcal{A}^{(1,2)} & \mathcal{B}^{(1,2)} \\ -\mathcal{B}^{(1,2)*} & -\mathcal{A}^{(1,2)*} \end{bmatrix} \begin{bmatrix} Y^{(2)} \\ Z^{(2)} \end{bmatrix} = \omega \begin{bmatrix} \mathcal{D} & 0 \\ 0 & \mathcal{D} \end{bmatrix} \begin{bmatrix} Y \\ Z \end{bmatrix} \tag{33a}$$

and

$$\begin{bmatrix} \tilde{\mathcal{A}}^{(1,2)*} & \tilde{\mathcal{B}}^{(1,2)} \\ -\tilde{\mathcal{B}}^{(1,2)*} & \tilde{\mathcal{A}}^{(1,2)} \end{bmatrix} \begin{bmatrix} Y \\ Z \end{bmatrix} + \begin{bmatrix} \mathcal{A}^{(2,2)} & \mathcal{B}^{(2,2)} \\ -\mathcal{B}^{(2,2)*} & -\mathcal{A}^{(2,2)*} \end{bmatrix} \begin{bmatrix} Y^{(2)} \\ Z^{(2)} \end{bmatrix} = \omega \begin{bmatrix} \mathcal{D}^{(2,2)} & 0 \\ 0 & \mathcal{D}^{(2,2)} \end{bmatrix} \begin{bmatrix} Y^{(2)} \\ Z^{(2)} \end{bmatrix} \tag{33b}$$

The dimensionality of the equations is determined by the number of 1p-1h and 2p-2h amplitudes included in the summations of Eq. (9) and (32). In Eqs. (33), the matrix elements of $\mathcal{A}$ and $\mathcal{B}$ are defined in Eqs. (21a) and the elements of $\mathcal{A}^{(1,2)}$, $\mathcal{B}^{(2,2)}$ are given by

$$\mathcal{A}^{(1,2)}_{m'\gamma';m\gamma,n\delta}(S) \equiv \langle 0 | [C_{m'\gamma'}(SM),\ H,\ \Gamma^{+}_{m\gamma,n\delta}(SM)] | 0 \rangle \tag{34a}$$

$$\mathcal{B}^{(1,2)}_{m'\gamma';m\gamma,n\delta} \equiv - \langle 0 | [C_{m'\gamma'}(SM),\ H,\ \Gamma_{m\gamma,n\delta}(\overline{SM})] | 0 \rangle \tag{34b}$$

$$\mathcal{A}^{(2,2)}_{m'\gamma',n'\delta';m\gamma,n\delta}(S) \equiv \langle 0 | [\Gamma_{m'\gamma',n'\delta'}(SM),\ H,\ \Gamma^{+}_{m\gamma,n\delta}(SM)] | 0 \rangle \tag{35a}$$

$$\mathcal{B}^{(2,2)}_{m'\gamma',n'\delta';m\gamma,n\delta}(S) \equiv - \langle 0 | [\Gamma_{m'\gamma',n'\delta'}(SM), H, \Gamma_{m\gamma,n\delta}(\overline{SM})] | 0 \rangle \tag{35b}$$

$$\mathcal{B}^{(2,2)}_{m'\gamma',n'\delta';m\gamma,n\delta}(S)\equiv\langle 0\,|\,[\,\Gamma_{m'\gamma',n'\delta'}(SM),\,\Gamma^{+}_{m\gamma,n\delta}(SM)]\,|\,0\rangle \qquad (36)$$

In Eqs. (33) we have dropped the state label S for convenience.

We now show how Eqs. (33) containing both 1p-1h and 2p-2h amplitudes are equivalent to a 1p-1h theory with a renormalized interaction. Hence to include the effect of double excitations on excitation energies we can renormalize the single excitation theory. It is obviously very important to recognize this in interpreting semi-empirical calculations. First, we note that the solution of Eq. (33b) for $Y^{(2)}$ and $Z^{(2)}$ involves the inverse of the matrix

$$\begin{bmatrix} \{\mathcal{A}^{(2,2)}-\omega\mathcal{B}^{(2,2)}\} & \mathcal{B}^{(2,2)} \\ -\mathcal{B}^{(2,2)*} & -\{\mathcal{A}^{(2,2)}+\omega\mathcal{B}^{(2,2)*}\} \end{bmatrix} \qquad (37a)$$

The inverse of the matrix Eq. (37a) has the form

$$\begin{bmatrix} \alpha & \beta \\ -\tilde{\beta}^{*} & -\delta^{*} \end{bmatrix} \qquad (37b)$$

with the properties

$$\tilde{\alpha}=\alpha^{*};\ \tilde{\delta}=\delta^{*} \qquad (37c)$$

The submatrices α, β, δ have the same dimensions of $\mathcal{A}^{(2,2)}$. We can now write

$$\begin{bmatrix} Y^{(2)} \\ Z^{(2)} \end{bmatrix} = -\begin{bmatrix} \alpha & \beta \\ -\tilde{\beta}^{*} & \delta^{*} \end{bmatrix}\begin{bmatrix} \tilde{a}^{*} & \tilde{b} \\ -\tilde{b}^{*} & -\tilde{a} \end{bmatrix}\begin{bmatrix} Y \\ Z \end{bmatrix} \qquad (38)$$

where $a \equiv \mathcal{A}^{(1,2)}$, $b \equiv \mathcal{B}^{(1,2)}$

With Eq. (38) the second term on the left hand side of Eq. (33a) becomes

$$\begin{bmatrix} a & b \\ -b^* & -a^* \end{bmatrix} \begin{bmatrix} Y^{(2)} \\ Z^{(2)} \end{bmatrix} = -\begin{bmatrix} \Delta_a & \Delta_b \\ -\tilde{\Delta}_{b^*} & -\Delta_{d^*} \end{bmatrix} \begin{bmatrix} Y \\ Z \end{bmatrix} \tag{39}$$

where

$$\Delta_a = a\alpha\tilde{a}^* + b\delta^*\tilde{b}^* - (a\beta\tilde{b}^* + b\tilde{\beta}^*\tilde{a}^*)$$

$$\Delta_d = a\delta\tilde{a}^* + b\alpha^*\tilde{b}^* - (a\tilde{\beta}\tilde{b}^* + b\beta^*\tilde{a})$$

$$\Delta_b = a\alpha\tilde{b} + b\delta^*\tilde{a} - (a\beta\tilde{a} + b\tilde{\beta}^*\tilde{b}) \tag{40}$$

Equation (33a) now reduces to an eigenvalue problem in the 1p-1h amplitudes only.

$$\begin{bmatrix} \underset{\sim}{\mathcal{A}}_1 & \underset{\sim}{\mathcal{B}} \\ -\underset{\sim}{\tilde{\mathcal{B}}}^* & -\underset{\sim}{\mathcal{A}}_2^* \end{bmatrix} \begin{bmatrix} Y \\ Z \end{bmatrix} = \omega \begin{bmatrix} \underset{\sim}{\mathcal{D}} & 0 \\ 0 & \underset{\sim}{\mathcal{D}}^* \end{bmatrix} \begin{bmatrix} Y \\ Z \end{bmatrix} \tag{41}$$

with

$$\begin{aligned} \underset{\sim}{\mathcal{A}}_1 &= \mathcal{A} - \Delta_a \\ \underset{\sim}{\mathcal{A}}_2 &= \mathcal{A} - \Delta_d \\ \underset{\sim}{\mathcal{B}} &= \mathcal{B} - \Delta_b \\ \underset{\sim}{\mathcal{D}} &= \mathcal{D} \end{aligned} \tag{42}$$

Note that α, β, and δ are functions of ω and hence so are $\mathcal{A}_1$, $\mathcal{A}_2$, and $\mathcal{B}$. In the 1p-1h approximation only the matrices $\mathcal{A}$ and $\mathcal{B}$ would appear in Eq. (41). The inclusion of 2p-2h excitations leads to a renormalized interaction implied in Eq. (42).

Since the effects due to 2p-2h components are expected to be small we can replace $|0>$ by $|HF>$ in evaluating the matrix elements $\mathcal{A}^{(1,2)}$ etc. Eqs. (34) - (36). In this approximation $\mathcal{B}^{0(1,2)}$ and $\mathcal{B}^{0(2,2)}$ vanish and

$$\alpha = (A^{0(2,2)} - \omega\, D^{0(2,2)})^{-1}$$

$$\delta^* = (A^{0(2,2)*} + \omega D^{0(2,2)*})^{-1}$$

$$\beta = 0 \tag{43}$$

With Eq. (43) Eqs. (40) become

$$\Delta_a = A^{0(1,2)}\ \alpha\ \tilde{A}^{0(1,2)*}$$

$$\Delta_d = A^{0(1,2)}\ \delta\ \tilde{A}^{0(1,2)*}$$

$$\Delta_b = 0 \tag{44}$$

If we further ignore the interaction terms in $A^{0(2,2)}$ it follows that

$$A^{0(2,2)}{}_{\gamma', n'\delta'; m\gamma, n\delta}(S) = (\epsilon_m + \epsilon_n - \epsilon_\gamma - \epsilon_\delta)\, D^{0(2,2)}{}_{m'\gamma', n'\delta'; m\gamma n\delta} \tag{45}$$

We can make the matrix $D^{0(2,2)}$ diagonal by choosing the 2p-2h creation

operators Γ^+ of Table I. The matrix elements of $A^{0(1,2)}$ in this basis are shown in Table II. With these elements we have

$$\{\Delta_a(\lambda 0)\}_{m'\gamma', n'\delta'} = \sum_{m\gamma} \frac{A^{0(1,2)}_{m'\gamma';m\gamma,m\gamma} A^{0(1,2)*}_{n'\delta';m\gamma,m\gamma}}{2(\epsilon_m - \epsilon_\gamma) - \omega(\lambda 0)}$$

$$+ \sum_{m<n} \sum_{\gamma} \frac{A^{0(1,2)}_{m'\gamma';m\gamma,n\gamma} A^{0(1,2)*}_{n'\delta';m\gamma,n\gamma}}{\epsilon_m + \epsilon_n - 2\epsilon_\gamma - \omega(\lambda 0)}$$

$$+ \sum_{m} \sum_{\gamma<\delta} \frac{A^{0(1,2)}_{m'\gamma';m\gamma,m\delta} A^{0(1,2)*}_{n'\delta';m\gamma,m\delta}}{2\epsilon_m - \epsilon_\gamma - \epsilon_\delta - \omega(\lambda 0)}$$

$$+ \sum_{m<n} \sum_{\gamma<\delta} \frac{A^{0(1,2)}_{m'\gamma',(m\gamma,n\delta)_1} A^{0(1,2)*}_{n'\delta',(m\gamma,n\delta)_1} A^{0(1,2)}_{m'\gamma';(m\gamma,n\delta)_2} A^{0(1,2)*}_{n'\delta';(m\gamma,n\delta)_2}}{\epsilon_m + \epsilon_n - \epsilon_\gamma - \epsilon_\delta - \omega(\lambda 0)} \tag{46}$$

for singlet states and

$$\{\Delta_a(\lambda 1)\}_{m'\gamma', n'\delta'} = \sum_{m<n} \sum_{\gamma} \frac{A^{0(1,2)}_{m'\gamma';(m\gamma,m\gamma)_2} A^{0(1,2)*}_{n'\delta',(m\gamma,m\gamma)_1}}{\epsilon_m + \epsilon_n - 2\epsilon_\gamma - \omega(\lambda 1)}$$

$$+ \sum_{m} \sum_{\gamma<\delta} \frac{A^{0(1,2)}_{m'\gamma';(m\gamma,m\delta)_2} A^{0(1,2)*}_{n'\delta';(m\gamma,m\delta)_2}}{2\epsilon_m - \epsilon_\gamma - \epsilon_\delta - \omega(\lambda 1)}$$

$$+ \sum_{m<n} \sum_{\gamma<\delta} [A^{0(1,2)}_{m'\gamma';(m\gamma,n\delta)_1} A^{0(1,2)*}_{n'\delta';(m\gamma,n\delta)_1} A^{0(1,2)}_{m'\gamma';(m\gamma,n\delta)_2} A^{0(1,2)*}_{n'\delta';(m\gamma,n\delta)_2}$$

Table IIa. Matrix Elements of $A^{0(1,2)}$ $(S = 0)$[a]

$$A^{0(1,2)}_{m'\gamma';m\gamma,m\gamma} = \sqrt{2}\,(\delta_{\gamma'\gamma}\,V_{\gamma m'mm} - \delta_{m'm}V_{\gamma\gamma m\gamma'})$$

$$A^{0(1,2)}_{m'\gamma';m\gamma,m\gamma} = \delta_{\gamma'\gamma}\,(V_{\gamma m'mn} + V_{\gamma m'nm}) - \delta_{m'm}V_{\gamma\gamma m\gamma'}$$

$(m \neq n)$

$$-\delta_{m'n}\,V_{\gamma\gamma m\gamma'}$$

$$A^{0(1,2)}_{m'\gamma';m\gamma,m\delta} = \delta_{\gamma'\gamma}V_{\delta m'mm} + \delta_{\gamma'\delta}\,V_{\gamma m'mm} - \delta_{m'm}(V_{\gamma\delta m\gamma'} + V_{\delta\gamma m\gamma'})$$

$(\gamma \neq \delta)$

$$A^{0(1,2)}_{m'\gamma';(m\gamma,n\delta)_1} = \frac{1}{\sqrt{2}}\{\delta_{\gamma'\gamma}(V_{\delta m'mn} + V_{\delta m'nm}) + \delta_{\gamma'\delta}(V_{\gamma m'mn} + V_{\gamma m'nm})$$

$(m\neq n,\ \gamma \neq\delta)$

$$-\delta_{m'm}(V_{\gamma\delta n\gamma'} + V_{\delta\gamma n\gamma'}) - \delta_{m'n}(V_{\gamma\delta m\gamma'} + V_{\delta\gamma m\gamma'})\}$$

$$A^{0(1,2)}_{m'\gamma';(m\gamma,n\delta)_2} = \sqrt{\frac{3}{2}}\{\delta_{\gamma'\delta}(V_{\gamma m'mn} - V_{\gamma m'nm})$$

$(m\neq n, \gamma \neq \delta)$

$$-\delta_{\gamma'\gamma}(V_{\delta m'mn} - V_{\delta m'nm})$$

$$+ \delta_{m'm}(V_{\gamma\delta n\gamma'} - V_{\delta\gamma n\gamma'})$$

$$-\delta_{m'n}(V_{\gamma\delta m\gamma'} - V_{\delta\gamma m\gamma'})$$

---

[a] These elements should be used in Eq. (46).

Table IIb. Matrix Elements of $A^{o(1,2)}$ $(S = 1)$[a]

$$A^{o(1,2)}_{m'\gamma';(m\gamma,m\gamma)_1} = -\delta_{\gamma'\gamma}(V_{\gamma m'mn} - V_{\gamma m'nm}) - \delta_{m'm} V_{\gamma\gamma m\gamma'}$$

$(m \neq n)$

$$+ \delta_{m'n} V_{\gamma\gamma m\gamma'}$$

$$A^{o(1,2)}_{m'\gamma';(m\gamma,n\delta)_1} = \frac{1}{\sqrt{2}}\{-\delta_{\gamma'\gamma}(V_{\delta m'mn} - V_{\delta m'nm})$$

$(m \neq n, n \neq \delta)$

$$-\delta_{\gamma'\delta}(V_{\gamma m'mn} - V_{\gamma m'nm}) - \delta_{m'm}(V_{\gamma\delta n\gamma'} + V_{\delta\gamma m\gamma'})$$

$$+\delta_{m'n}(V_{\gamma\delta m\gamma'} + V_{\delta\gamma m\gamma'})\}$$

$$A^{o(1,2)}_{m'\gamma';(m\gamma,m\delta)_2} = \delta_{\gamma'\gamma} V_{\delta m'mm} - \delta_{\gamma'\delta} V_{\gamma m'mm}$$

$(\gamma \neq \delta)$

$$+ \delta_{m'm}(V_{\gamma\delta m\gamma'} - V_{\delta\gamma m\gamma'})$$

$$A^{o(1,2)}_{m'\gamma';(m\gamma,n\delta)_2} = \frac{1}{\sqrt{2}}\{\delta_{\gamma'\gamma}(V_{\delta m'mn} + V_{\delta m'nm})$$

$(m \neq n; \gamma \neq \delta)$

$$-\delta_{\gamma'\delta}(V_{\gamma m'mn} + V_{\delta m'nm})$$

$$+\delta_{m'm}(V_{\gamma\delta m\gamma'} - V_{\delta\gamma m\gamma'}) + \delta_{m'n}(V_{\gamma\delta m\gamma'} - V_{\delta\gamma m\gamma'})\}$$

$$A^{o(1,2)}_{m'\gamma';(m\gamma,n\delta)_3} = -\delta_{\gamma\gamma'}(V_{\delta m'mn} - V_{\delta m'nm})$$

$(m \neq n, \gamma \neq \delta)$

$$+\delta_{\gamma'\delta}(V_{\gamma m' mn} - V_{\gamma m' nm}) + \delta_{m' m}(V_{\gamma \delta n\gamma'} - V_{\delta\gamma n\gamma'})$$

$$-\delta_{m' n}(V_{\gamma \delta m\gamma'} - V_{\delta\gamma m\gamma'})$$

---

[a] These elements should be used in Eq. (47).

$$A^{0(1,2)}_{m'\gamma'}(m\gamma, n\delta)_3 A^{0(1,2)}_{n'\delta'};(m\gamma, n\delta)_3]/[\epsilon_m + \epsilon_n - \epsilon_\gamma - \epsilon_\delta - \omega(\lambda 1)] \tag{47}$$

for triplet states. To obtain the matrix elements of $\Delta_d(\lambda S)$ one replaces $-\omega(\lambda S)$ by $+\omega(\lambda S)$ in Eqs. (46) and (47). In this approximation the matrices Δ_a and Δ_d are no longer equal and hence $\underset{\sim}{\mathcal{X}}_1$ and $\underset{\sim}{\mathcal{X}}_2$ are not the same. The matrix equation Eq. (41) will not have the symmetry of the original 1p-1h theory, Eq. (21). The simplest way around this difficulty is to treat that part of the matrix containing the effects of 2p-2h states as a perturbation on the 1p-1h theory. We then have for the excitation frequency, ω,

$$\omega = \omega^{(1p\text{-}1h)} - \Delta\omega \tag{48}$$

with $\Delta\omega$ given by perturbation theory

$$\Delta\omega \simeq \tilde{Y}^* \Delta_a Y + \tilde{Z}^* \Delta_d^* Z + \tilde{Y}^* \Delta_b Z + Z^* \Delta_b^* Y \tag{49}$$

Y and Z are the amplitudes obtained in the 1p-1h approximation and Δ_a, Δ_b, and Δ_d are evaluated using the corresponding frequency. With the approximation Eq. (44) Eq. (49) reduces to

$$\Delta\omega \simeq \tilde{Y} \quad \Delta_a \tilde{Y} + \tilde{Z}^* \quad \Delta_d^* Z \tag{50}$$

Also Z is much smaller than Y and Δ_d is also small compared to Δ_a and hence we can neglect the second term on the right hand side of Eq. (50) and use the Y amplitudes of the TDA. This is just the energy lowering of the excited state due to double excitations.

CONCLUSIONS

We have discussed the equations-of-motion method as an approach to calculating excitation energies and transition matrix elements of excited states directly as opposed to the conventional approach of obtaining the total energies and wavefunctions of the stationary states of the total Hamiltonian. We have extended our proposed solution of Rowe's variational form of the equation of motion[1] - referred to as a higher random phase approximation[4] - in two ways. First we include the proper renormalization of the equations with respect to the ground state particle-hole densities. These equations now contain renormalized matrix elements but have the same matrix form as the RPA. We have shown that the corrections to the transition energies due to this renormalization are small.[13]

We have also shown how to include the effects of two-particle-hole contributions in the excited states. The single-particle-hole amplitudes are by far the most important in the excitation operator but doubly excited configurations can affect the excitation energies by as much as two to three volts. An important conclusion of this section is that the theory with single-and two-particle-hole states can be shown to be equivalent to a single particle-hole theory with a renormalized interaction. Some of these conclusions have been obtained previously using either the quasi-boson approximations or time-dependent variational methods.[15] Our approach on the other hand, starts from Rowe's equations,[1] enabling us to derive more general

equations, Eq. (41).

We have applied the theory developed in this paper and reference 4 extensively to the excited states of nitrogen, carbon monoxide, ethylene, butadiene, and benzene. A comparison of the calculated results for N_2 and CO with experiment shows that the theory can predict excitation energies and transition moments accurately and economically.[13]

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[15] See reference 1 for references other than reference 8.